

CONCLUSION

In light of the foregoing, Applicants respectfully submit that all claims are now in condition for allowance.

If the Examiner believes that a telephone conversation with Applicants' attorney would expedite allowance of this application, the Examiner is cordially invited to call the undersigned attorney at (617) 570-1806.

A check for \$1020 and a petition for a three-month extension of time are enclosed. Applicants believe that no additional fees are required. However, if any other fee is due, please charge any such fee occasioned by this paper to our Deposit Account No. 07-1700.

Respectfully submitted,

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Vol. 7

DENTAL MATERIALS 961

acrylates, some containing relatively high loadings of fillers, such as fine glass powders.

Resin cements have excellent aesthetic qualities and are essentially insoluble in mouth fluids. Compressive strength is low, but can be increased by the addition of fillers. They have no inherent adhesion to the tooth. Retention is dependent on mechanical locking when the cement flows into irregularities on the surfaces of the substances being cemented.

Resin cement materials are provided as a two-part powder-liquid product. The powder consists largely of poly(methyl methacrylate) to which various fillers (qv) may be added. These include calcium carbonate [471-34-1], silica [7631-86-9], barium carbonate [513-77-9], and calcium tungstate [7790-75-2]. An organic peroxide, eg, benzoyl peroxide, capable of generating free radicals is also present (see INITIATORS; PEROXIDES, ORGANIC).

The liquid is basically a methacrylate monomer having a suitable inhibitor to ensure adequate shelf life. *N,N'*-Dimethyl-p-toluidine [99-97-8] is probably the most common polymerization accelerator although *N,N*-bis(2-hydroxyethyl)-p-toluidine and/or a sulfinate salt, eg, sodium *p*-toluene sulfinate [873-55-2], also may be used.

Fluid, free-radical polymerizable resin-based cements based on the use of cross-linking monomer systems, eg, BIS-GMA and urethane dimethacrylates, having small particulate fillers, yield strong, insoluble materials suitable for cementation applications, eg, crowns, bridges, composites. Bonding is by penetration into etched or roughened surfaces of the substrate. The use of surface active monomers, such as are being used in dentin adhesive systems, eg, 4-methacryloyloxy trimellitic anhydride (4META), have been successfully used in resin cement formulations.

Visible light activated resin compositions containing calcium hydroxide have been made available as cavity lining materials (99) for pulp capping and pulpotomy, and may offer in other applications an alternative to the calcium salicylate type cements.

Dental Plasters

Gypsum is widely distributed naturally as calcium sulfate dihydrate [10101-41-4], $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. When partially calcined, the hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, is formed (see CALCIUM COMPOUNDS—CALCIUM SULFATES). Gypsum has been used in one form since 1756 for making dental casts, and in another form since 1844 for dental impressions (101).

Plaster is the rehydrated calcined gypsum. The American Dental Association classifies five types of dental plaster according to the physical properties: type I, impression plaster; type II, model plaster; type III, dental stone; type IV, high-strength dental stone; and type V, high-strength, high-expansion dental stone. These different types are the result of various calcining methods.

Although plaster has been a very successful and serviceable material, it is seriously lacking in hardness, edge strength, chip resistance, abrasion resistance, and strength to fulfill many needs of dentistry. Some of these requirements have

been partially filled by the development of the type III and type IV plasters. Table 3 lists the compression strength of dental plasters.

To form plaster, gypsum is ground and subjected to temperatures of 110–120°C in open kettles to drive off part of the water of crystallization. The crystals thus formed are large and porous and are the type I and type II plasters. These crystals require a 2:1 powder-gauging water ratio for proper consistency. Type I, impression plaster, and type II, model plaster, differ in additives that control working and setting times. When gypsum is formed these crystals form the type III plaster commonly called dental stone and require 28–35 mL of water for 100 g of powder. Type IV, high-strength dental stone is formed by calcining gypsum in a 30% solution of calcium chloride. The crystals resulting from this process are slightly larger and denser than the type II crystals and require even less gauging water (20–22 mL/100 g of powder). Type V dental stone has gypsum that is formed by a process similar to that for the type IV stone, with the use of calcium chloride. Additives, such as fillers and surface tension reducing chemicals, result in higher setting expansion and higher strength. Hence, less gauging water is required, ie, only 18–20 mL/100 g is needed.

Although gypsum products develop a linear expansion during hardening, the true volume of the final dihydrate is ca 7% less (103,104) than the total volume of the hemihydrate plus the water required for the chemical conversion of the

Table 3. Compressive Strength of Dental Plasters, Investments

Materials	Compressive strength, MPa ^{a,b}	ISO standard no.
<i>Plasters</i>		
impression	4.0 ^c –8.0 ^d	6873
model	9.0 ^e	6873
dental stone	20 ^f	6873
high-strength dental stone	35 ^g	6873
<i>Investments</i>		
inlay and crown ^h	2.3 (1.7)	7490
partial denture ⁱ	5.8 (3.3)	7490
phosphate-bonded ^{j,k}	3.0	7490
ethyl silicate-bonded ^j	1.5	proposed
<i>Dies</i>		
gypsum refractory	13.0	proposed
phosphate refractory	13.0	proposed

^aTo convert MPa to psi, multiply by 145.

^bValue given is at room temperature. Value in parenthesis is at casting temperature.

^cValue given is minimum value.

^dValue given is maximum value.

^eLow temperature casting investments.

^fHigh temperature casting investments.

^gRef. 102.

hemihydrate to hydrate. In order to produce a pourable consistency, an excess of water is always used. As the gypsum crystals grow in the form of needlelike projections from each center of crystallization, these growing spiny shapes floating in an excess of water push themselves apart from each other. Voids form between the growing crystals which ultimately interlock to make the mass rigid and hard. Setting expansion is a result of this apparent increase in volume owing to the formation of voids.

As a result of the linear expansion, the reduced volume of the dihydrate, and the evaporation of excess water, the percentage of void spaces in plaster is ca 45%, in stone 15%, and in improved stone 10%. Thus, the additional amount of water required for plaster contributes to the volume but not to the strength of the hardened material (105).

Each 100 g of calcined gypsum theoretically requires only 18.6 mL of water to complete the chemical reaction from the hemihydrate to the dihydrate. Any amount of water greater than 18.6 mL/100 g of powder is excess and reduces the strength of the hardened plaster. When a mixture of the hemihydrate and water hardens, linear expansion takes place. This expansion may amount to as much as 0.5% for plaster. Dental stones also expand on setting, but the amount is significantly less than that permitted in plaster, ie, 0.2% for type III, 0.1% for type IV, and 0.3% for type V.

Impression Plasters. Impression plasters are prepared by mixing with water. Types I and II plasters are weaker than dental stone (types III and IV) because of particle morphology and void content. There are two factors that contribute to the weakness of plaster compared to that of dental stone. First, the porosity of the particles makes it necessary to use more water for a mix, and second, the irregular shapes of the particles prevent them from fitting together tightly. Thus, for equally pourable consistencies, less gypsum per unit volume is present in plaster than in dental stone, and the plaster is considerably weaker.

Impression plasters are formulated to produce a thin, fluid slurry when mixed with the proper amount of water. A satisfactory impression plaster should have a setting time of 4 ± 1.5 min; fineness, ie, 98% should pass a number 100 sieve (ca 0.15 mm), and 90% pass a number 200 sieve (ca 0.07 mm); setting expansion at 2 h should be $<0.15\%$; the compressive strength at one hour should be 5.9 ± 2 MPa (855.5 ± 290 psi); and testing consistency as determined by the diameter of the slump in the consistence test should be 90 ± 3 mm.

Impression plasters are manufactured from the finest finishing plasters, selected for color and purity. Setting time accelerators, setting expansion control agents, fillers, flavors, colors, or other special modifying agents may be added, eg, starch, to cause disintegration of the plaster impression when it is boiled.

Impression plasters are used to obtain an impression (or negative) of the hard and soft tissues of the mouth. The plaster slurry is placed in a tray, inserted into the mouth, pressed in place against the area in question, and held still until it hardens.

Model Plasters. Model plaster should have a setting time of approximately 10 minutes. The fineness of the powder should be such that 98% passes a number 100 sieve (ca 0.15 mm) and 90% passes a number 200 sieve (ca 0.07 mm). Setting expansion should be less than 0.30%, compressive strength at the end of one h

should be a minimum of 8.8 MPa (1276 psi), and the consistency should form a disk during the slump test of 30 ± 2 mm diameter.

Model plasters are manufactured from select finishing plasters with special emphasis on a clean, white color. Setting-time control agents, setting-expansion control additives, fillers, and pigments may be added.

After it is mixed in water, model plaster is poured into an impression (negative) to produce a cast (positive) or oral structure. This plaster cast is produced chiefly for study or record purposes, ie, successive casts allow an orthodontist to follow and demonstrate the results of corrective treatment. Additional uses for model plaster include the making of study casts and denture repair casts; mounting interarch registration assemblies on articulators; flasking dentures during processing; and for a variety of other applications where strength and abrasion resistance are not of prime importance.

Dental Stones. Dental stones, produced from gypsum, are sold as dry powders in sealed containers. They are prepared for use by mixing with water, in proportions recommended by the manufacturer.

Dental stone is generally used at a water-powder volume ratio of about 30 parts water to 100 parts of stone. The mix is not easily poured, but can flow readily under mechanical vibration. The physical property requirements include a setting time of 10 ± 3 min; fineness of powder, where 98% should pass a number 100 sieve (ca 0.15 mm) and 90% pass a number 200 sieve (ca 0.07 mm); linear setting expansion at 2 h of $<0.20\%$; compressive strength at 1 h of 20.6 MPa (2987 psi); and consistency such that the slump test disk is 30 ± 2 mm diameter.

Setting-time control agents, setting-expansion control agents, fillers, colors, or other modifying additions may be added. Calcium sulfate dihydrate and sodium chloride [7647-14-5] are effective accelerators. Potassium sulfate [7778-80-5] and sodium potassium tartrate [304-59-6] accelerate the setting rate and decrease the setting expansion. Borax [1303-96-4], potassium carbonate [584-08-7], sodium carbonate [497-19-8], and sodium citrate [68-04-2] are all effective retarders and reduce the setting expansion.

Type III dental stones are used for casts requiring higher compressive strength and abrasion resistance than casts formed using the type II plaster. These dental casts are used for the processing of denture-base materials.

High Strength Dental Stone. This dental stone is often referred to as improved dental stone. The crystals are of a cubic or rectangular shape and show a reduction in cracking and porosity. These changes in crystals reduce the amount of water required to wet the powder and produce a workable consistency, ie, 20–22 parts water per 100 parts powder.

Mixes of improved dental stone (type IV) using 22 parts of water to 100 parts of powder produce a mass that is not fluid and pourable but can be easily vibrated into place. The physical properties of the improved dental stone include a setting time 10 ± 3 min, fineness of powder such that 98% passes a 100 sieve (ca 0.15 mm) and 90% passes a 200 sieve (ca 0.07 mm); setting expansion at 2 h limited to a max of 0.10%; compressive strength at 1 h of at least 34.3 MPa (4974 psi); and a disk formed in the slump test for consistency of a 30 ± 2 mm diameter.

Type IV dental stones are used to make casts for a single tooth, for crown or inlay work, and for a complete dental arch.

High Strength, High Expansion Dental Stone. This is a die stone intended for the developments in techniques, materials, and approaches to clinical dentistry that require the higher expansion attainable with model plaster and even higher strength than type IV dental stone. The setting time is 12 ± 4 minutes; the compressive strength must be no lower than 48 MPa (6960 psi); and the setting expansion must lie between 0.10 and 0.30%.

Type V dental stone is used for making dies employed in the fabrication of wax patterns for prostheses cast in nonprecious dental alloys. Nonprecious dental alloys generally solidify at higher temperatures than the high noble and precious metal alloys and have more shrinkage as they cool to room temperature. The higher expansion of type V dental stone provides a larger die and, as a result, a larger pattern that compensates for the greater shrinkage of the casting. Type V stone is a possible choice whenever compensation for more shrinkage of a prosthetic or other material, such as a duplicating material or impression material, is needed.

Dental Investments

Dental investments are comprised of refractory materials capable of withstanding elevated temperatures. They are used as casting investments and model investments. The compressive strengths, according to International Standards, of the investments and die materials are shown in Table 3.

Casting Investments. Casting investments are used to form molds into which molten metal may be cast. The cavity for receiving the metal is formed by the lost wax process. The composition of investments used for alloys cast from low ($\leq 1100^{\circ}\text{C}$) temperatures are different from those used for alloys cast from higher ($\geq 1300^{\circ}\text{C}$) temperatures.

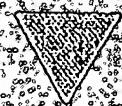
A casting investment must provide sufficient expansion to compensate for shrinkage (up to 0.4%) of the wax (or plastic) pattern during its fabrication, and shrinkage (1.2–2.0%) of the cast alloys resulting from solidification and cooling. The higher the solidification temperature of an alloy the greater is its casting shrinkage.

The compensating expansion of a dental investment may be separated into two types, setting and thermal. Setting expansion includes expansion or dimensional change from the curing of the investment, and expansion from excessive water in contact with the investment after its original mixing with recommended water (106,107). This water may be added by either immersion of the mixed investment in a water bath or as an excess of water from a presoaked porous ceramic liner, called a casting ring, that is placed between the mixture and a metal cylinder container. Thermal expansion is caused by the expansion of the set investment during heating through a wax burnout process and by changes of some component(s) of the investment to lower density phases at the elevated temperatures (108).

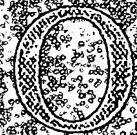
Investments for Low-Temperature ($T \leq 1100^{\circ}\text{C}$) Casting Alloys. Low temperature casting alloys are usually comprised of gold, silver, and copper and are used for inlays, crowns, and removable partial dentures. At the temperature tested, the compressive strengths specified for inlay or partial denture investments are

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Gypsum Products

Chemistry of Setting, Basic Principles, and Technical Considerations

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 - Dental Plaster and Stone
 - Setting of Gypsum Products
 - Tests for Working, Setting, and Final Setting Times
 - Control of the Setting Time
 - Setting Expansion
 - Accelerators and Retarders: Practice and Theory
 - Hygroscopic Setting Expansion
 - Strength
 - Types of Gypsum Products
 - Proportioning, Mixing, and Caring for Products
 - Infection Control Concerns
-

USES OF GYPSUM IN DENTISTRY

Gypsum is a mineral that is mined in various parts of the world. It is also a by-product of some chemical-processing operations. Chemically, the gypsum that is produced for dental purposes is nearly pure calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Different forms of gypsum have been used for many centuries for construction purposes. It is assumed that the alabaster used in the building of King Solomon's temple of biblical fame was a form of gypsum. Products made from gypsum are widely used in industry, and practically all homes and buildings have walls of plaster.

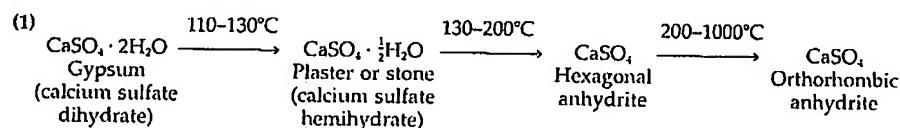
Gypsum products are used in dentistry for the preparation of study models for oral and maxillofacial structures and as important adjuncts to dental laboratory operations that are involved in the production of dental prostheses. Various types of plaster are used to form molds and casts on which dental prostheses and restorations are constructed. When the plaster is mixed with silica, it is known as *dental investment*. Such dental investments are used to form molds for the casting of dental restorations with molten metal, and they are discussed at

length in Chapter 22. The present discussion is confined to the relatively pure gypsum products, such as plaster, that harden when mixed with water.

The use of gypsum in dentistry is widespread. Its use can be demonstrated in the preparation of a cast for a denture. A mixture of plaster of Paris and water is placed in an *impression tray* and pressed against the tissues of the jaw, for example. The plaster is allowed to harden, or *set*, and then the impression is withdrawn. The dentist now has a *negative* form of these tissues that was made within the oral cavity. If another variety of plaster known as *dental stone* is now mixed with water, poured into the impression, and allowed to set, the hardened plaster impression serves as a mold to form a positive model, or master cast. It is on this cast that the denture is constructed, without the patient being present.

DENTAL PLASTER AND STONE

Production of Calcium Sulfate Hemihydrate. These materials are the results of the calcining of calcium sulfate dihydrate, or gypsum. Commercially, the gypsum is ground and subjected to temperatures of 110° to 120° C (230° to 250° F) to drive off part of the water of crystallization. This corresponds to the first step in reaction (1). As the temperature is further raised, the remaining water of crystallization is removed, and products are formed as indicated.



The principal constituent of the dental plasters and stones is the calcium sulfate hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) (or $\text{CaSO}_4 \cdot \text{H}_2\text{O}$). Depending on the method of calcination, different forms of the hemihydrate can be obtained. These forms are referred to as α -hemihydrate or β -hemihydrate. The use of α and β prefixes suggests two phases from the point of view of the phase rule, but this is not the case. Although the α and β designations are continued in this edition because of tradition and convenience, it should not be inferred that there are mineralogic differences between them. The differences between α - and β -hemihydrates are a result of differences in crystal size, surface area, and degree of lattice perfection. In reality, the β form is a fibrous aggregate of fine crystals with capillary pores, whereas the α form consists of cleavage fragments and crystals in the form of rods or prisms.

If gypsum is heated to the temperatures indicated in the first part of reaction 1 in a kettle, vat, or rotary kiln open to the air, a crystalline form of the hemihydrate is produced. As can be seen in Figure 9-1, the β -hemihydrate crystals are characterized by their "sponginess" and irregular shape. In contrast the α -hemihydrate (stone) crystals, the α -hemihydrate (stone) crystals are more dense and have a prismatic shape. Powder particles of dental stone (α -hemihydrate) are shown in Figure 9-2.

Different procedures can be employed to obtain the hemihydrate. The product of these processes is the principal constituent of the dental stones from which casts and models are made. When the α -hemihydrate is mixed with water, reaction 1 is reversed, as described in the next section, and the product obtained is one much stronger and harder than that resulting from β -hemihydrate. The chief reason for this difference is that the α -hemihydrate powder requires much

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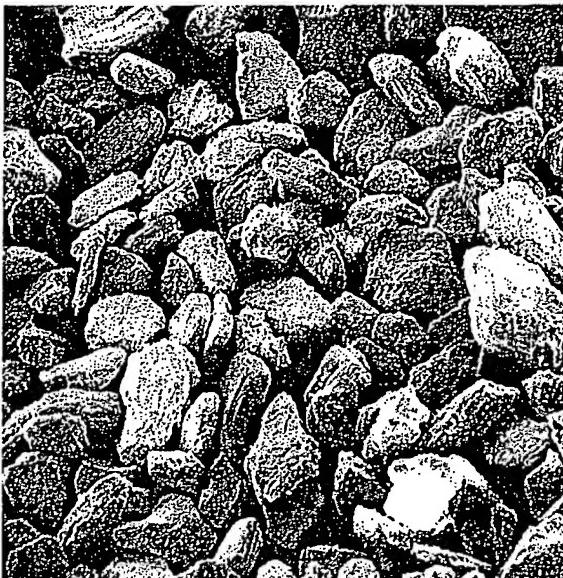


Figure 9-1. Powder particles of plaster of Paris (β -hemihydrate). Crystals are spongy and irregular in shape. $\times 400$. (Courtesy of B. Giannara and R. Neiman.)

less water when it is mixed than does the β -hemihydrate. The β -hemihydrate requires more water to float its powder particles so that they can be stirred, because the crystals are more irregular in shape and are porous in character.

Although particle size and the total surface area are the chief factors in determining the amount of gauging water, the particle size distribution also plays an important role. The grinding of the particles after the preparation of the hemihydrate can eliminate needlelike crystals and provide better packing characteristics, hence lowering the amount of mixing water required.

Adhesion between the particles of hemihydrate is also a factor in determining



Figure 9-2. Powder particles of dental stone (α -hemihydrate). Crystals are prismatic and more regular in shape than those of plaster. The very fine particles that are normally present have been removed, as was done for the plaster particles in Figure 9-1. $\times 400$. (Courtesy of B. Giannara and R. Neiman.)

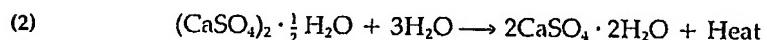
the amount of water required to produce a product that can be poured. Small amounts of some surface-active materials, such as gum arabic plus lime, added to the hemihydrate can reduce markedly the water requirements of both plaster and dental stone.

From the preceding description, it is clear that various gypsum products require different amounts of water and that these differences are accounted for principally by shape and compactness of the crystals. These factors are regulated by the manufacturer and are dependent on the type of process used, dehydration temperatures, particle size of the gypsum to be calcined, length of calcination, time of grinding of finished product, and addition of surface active ingredients to the final product.

Commercial Gypsum Products. The various plasters and stones that are available commercially consist of one of the forms of hemihydrate. Because they are processed products, however, they contain additional small amounts of impurities, unconverted hexagonal or orthorhombic anhydrites. Additional gypsum and other salts may also be added to control the setting time and expansion, as discussed in later sections.

SETTING OF GYPSUM PRODUCTS

Reaction 1 described the sequence for calcining calcium sulfate dihydrate to form calcium sulfate hemihydrate, the starting material used for production of gypsum casts, models, certain casting investments, and impression plasters. This reaction can be reversed as follows:



The product of the reaction is gypsum, and the heat evolved in the exothermic reaction is equivalent to the heat used originally in calcination.

The products formed during calcination all react with water to form gypsum, but at different rates. For example, hexagonal anhydrite reacts very rapidly, whereas the reaction may require hours when orthorhombic anhydrite is mixed with water. This is caused by the fact that the orthorhombic anhydrite has a more stable and closely packed crystal lattice.

Setting Reactions. Nature has provided us with a unique material in gypsum. The various hydrates have a relatively low solubility with a distinct difference in the solubility of the hemihydrate and the dihydrate. The dihydrate is too soluble for use in structures exposed to the atmosphere, which is probably fortunate, because such usage would long ago have exhausted our natural supply of gypsum.

In Figure 9-3 it can be seen that the hemihydrate is four times more soluble in water than is the dihydrate near room temperature (20° C). Thus, the setting reactions can be understood as follows:

1. When the hemihydrate is mixed with water, a suspension is formed that is fluid and workable.
2. The hemihydrate dissolves until it forms a saturated solution.
3. This saturated hemihydrate solution is supersaturated with dihydrate, so the latter precipitates out.

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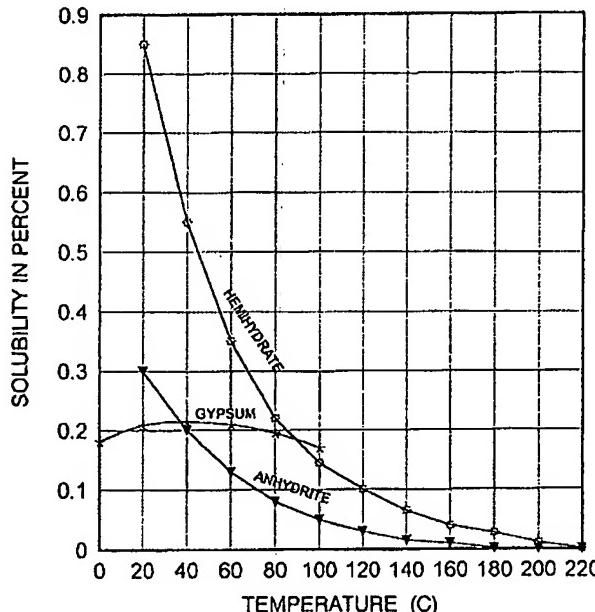


Figure 9-3. Equilibrium diagram of calcium sulfate and water between 0° and 220° C.

4. As the dihydrate precipitates, the solution is no longer saturated with the hemihydrate, so it continues to dissolve. Thus, the process continues, that is, dissolution of the hemihydrate and precipitation of the dihydrate occur as either new crystals form or further growth occurs on those already present. The reaction is continuous and proceeds until no further dihydrate precipitates out of solution. The anhydrite is not formed in aqueous media.

The curves from a plot of heat rise (or temperature) during setting as a function of time are similar in shape to those shown in Figure 9-9 (discussed later) for compressive strength as a function of time. The peak is reached earlier or later, depending on the setting time. The mass will begin to cool in 5 to 15 minutes, but the reaction and strengthening process may continue slowly for hours.

The effect of varying the water:powder (W:P) ratio is best illustrated by measuring the crushing (compressive) strength that develops. Figure 9-4 shows a plot of the strength values that have been measured for the five different types of gypsum products as a function of the W:P ratio. The products represented in Figure 9-4 cover the wide range of gypsum products that are used in dentistry. The figure includes data from many of the products on the market that meet American Dental Association (ADA) Specification No. 25 for dental gypsum products and the strength values represent the *wet strength* at 1 hour. The strength values increase as the specimens dry and may double in a week.

As the amount of gypsum increases during the setting period, the mass thickens because of the formation of needlelike crystals as shown in Figure 9-5. When a lower W:P ratio is used, the crystals become broader and, through intergrowth, they form a strong, solid mass. At a W:P ratio near the theoretical limit of 0.18, some of the hemihydrate crystals do not fully dissolve, but they hydrate and still tend to harden the structure.

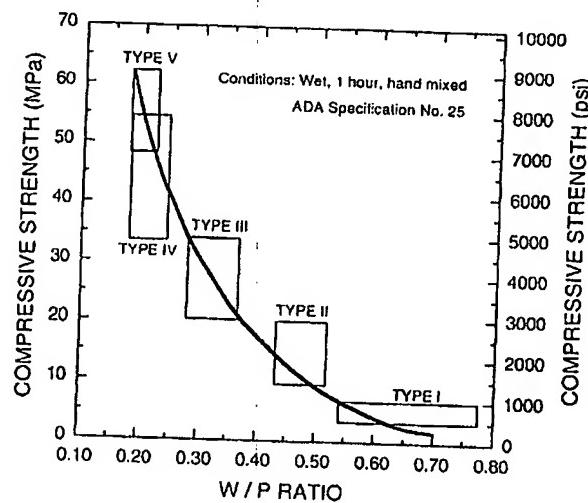


Figure 9-4. Compressive strength as a function of W:P ratio for the five types of gypsum products.

W:P Ratio. The amounts of water and hemihydrate should be gauged accurately by weight. The ratio of the water to the hemihydrate powder is usually expressed as the water:powder ratio, or the quotient obtained when the weight (or volume) of the water is divided by the weight of the powder. The ratio is usually abbreviated as W:P. For example, if 100 g of plaster is mixed with 60 mL of water, the W:P ratio is 0.6; if 100 g of dental stone is mixed with 28 mL of water, the W:P ratio is 0.28. The W:P ratio is an important factor in determining the physical and chemical properties of the final gypsum product. For example, the higher the W:P ratio, the longer the setting time and the weaker is the gypsum product. Although the W:P ratio varies for the particular brand of plaster or stone, the following are some typical recommended ranges: Type II plaster, 0.45 to 0.50; Type III stone, 0.28 to 0.30; and Type IV stone, 0.22 to 0.24.

TESTS FOR WORKING, SETTING, AND FINAL SETTING TIMES

Mixing Time. This is the time from the addition of the powder to the water until mixing is completed. Mechanical mixing of stones and plasters is usually

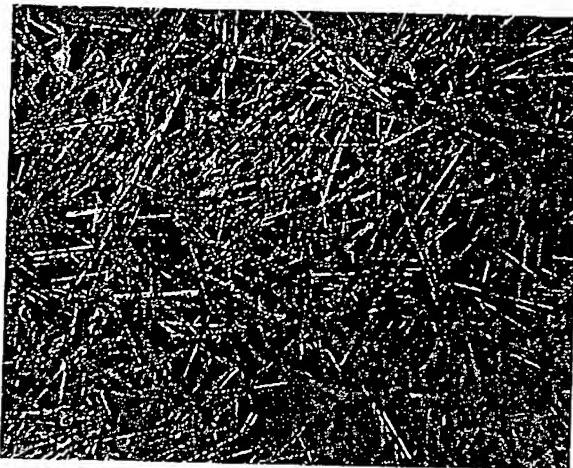


Figure 9-5. Dark-field photomicrograph of set plaster mixed with excess water to prevent the field from becoming opaque. $\times 200$.

completed in 20 to 30 seconds. Hand spatulation generally requires at least a minute to obtain a smooth mix.

Working Time. This is the time available to use a workable mix, one that maintains an even consistency that may be manipulated to perform one or more tasks. For example, sufficient working time might be needed to pour an impression, pour a spare impression, and clean the equipment before the gypsum fully sets. Generally, a 3-minute working time is adequate.

Setting Time. Reaction 2 requires a definite time for completion. The powder is mixed with water, and the time that elapses from the beginning of mixing until the material hardens is known as the *setting time*. This is usually measured by some type of penetration test, using the instruments in Figure 9-6. One normally thinks of this as a certain time in minutes as stated on the package label. Actually, there are a number of stages in the setting of a gypsum product, as described by use of an actual strength test on a dental model plaster (Fig. 9-7). In Figure 9-7, 1 minute is indicated for mixing (MT), with an additional 3 minutes for working (WT), that is, pouring into an impression.

Loss of Gloss Test for Initial Set. As the reaction proceeds, some of the excess water is taken up in forming the dihydrate so that the mix loses its gloss (LG). In the example shown, this occurred at approximately 9 minutes, and the mass

Figure 9-4. Compressive strength function of W:P ratio for the types of gypsum products.

ould be gauged accurately. The water:powder ratio is usually obtained when the weight of the powder. The ratio is 1.0 for Type I plaster when mixed with 60 mL of water. When mixed with 28 mL of water, the water:powder ratio factor in determining the compressive strength of the product. For example, the greater the water:powder ratio, the weaker is the product. The particular brand of plaster has recommended ranges: Type II plaster, 0.20 to 0.22; Type IV plaster, 0.22 to 0.24.

The water:powder ratio for the various types of gypsum products is usually

Figure 9-5. Dark-field photomicrograph of set plaster mixed with excess water to prevent the field from becoming opaque. $\times 200$.

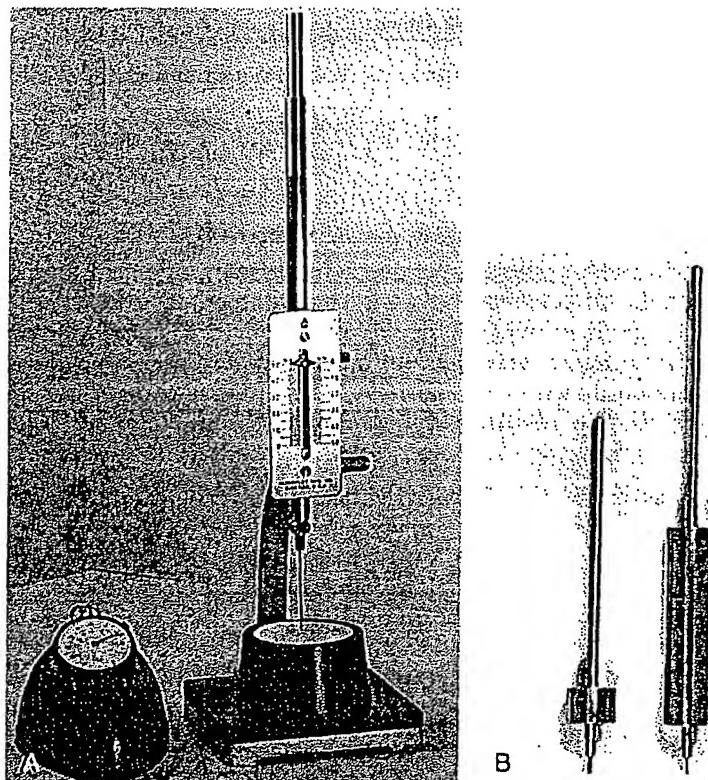


Figure 9-6. A, Vicat needle being used to measure the setting time of a gypsum product. The setting time is the elapsed time from the start of mix until the needle no longer penetrates to the bottom. B, Set of Gillmore needles.

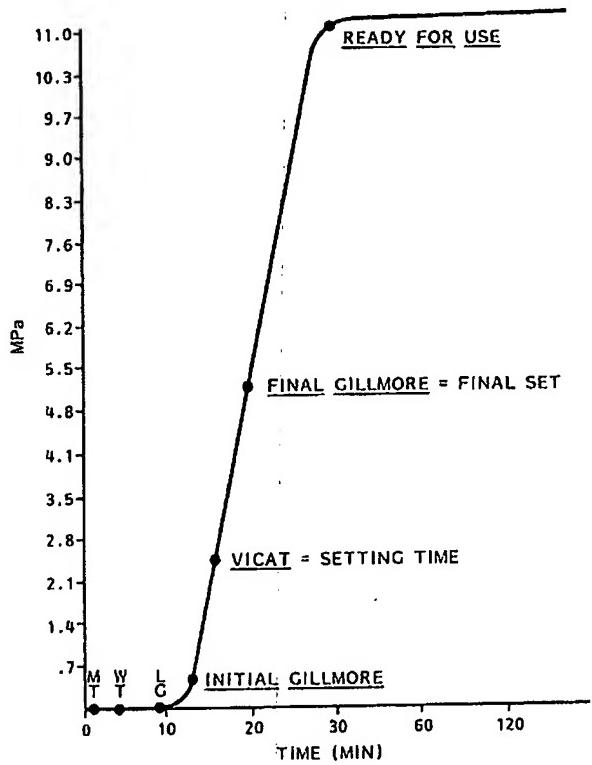


Figure 9-7. Compressive strength of a Type-II model plaster during setting. The W:P ratio was 0.50. The various stages in the setting reaction are indicated by the particular instruments used in measuring the hardening of the mix. MT, mixing time; WT, working time; and LG, loss of gloss from the surface of the mix.

still had no measurable compressive strength. Therefore, it could not be safely removed from the mold.

Initial Gillmore Test for Initial Set. At the right of Figure 9-6 are shown two Gillmore needles. The smaller one is most frequently used for testing the setting time of dental cements, but it is sometimes used on gypsum products. The mixture is spread out. The needle is lowered onto the surface, and the time at which it no longer leaves an impression is called the *initial set*, noted at Initial Gillmore on the curve in Figure 9-7. This time is marked by a definite increase in strength. The initial set in the example seen in Figure 9-7 is 13 minutes.

Vicat Test for Setting Time. Another instrument is used to determine the next stage in the reaction, the Vicat penetrometer seen on the left in Figure 9-6. The needle with a weighted plunger rod is supported and is held just in contact with the mix. Soon after the gloss is lost, the plunger is released. The time elapsed until the needle no longer penetrates to the bottom of the mix is known as the *setting time*. In some cases, the Vicat and Initial Gillmore measurements occur at the same time, whereas in others there is a small difference, as shown.

Gillmore Test for Final Setting Time. The next stage in the setting process may be measured by the use of the heavier Gillmore needle. The elapsed time when it leaves only a barely perceptible mark on the surface is called the *final setting time*. It is rarely used as an indication of the ready-for-use stage.

Ready-for-Use Criterion. This is a subjective measure of the time at which the set material may be safely handled in the usual manner. There is no designated test, but the ability to judge readiness improves with experience. Technically, it may be considered as the time when the compressive strength is at least 80% of that attained at 1 hour. Most modern products reach the ready-for-use state in 30 minutes (see Fig. 9-7).

The preceding illustrates the stages in the setting of gypsum products. The figures are for one typical model plaster, but they vary, depending on each product, the W:P ratio, and the time of mixing. Only the Vicat setting time is listed under tables of physical properties. Although manufacturers have developed their own tests for working time, the Vicat test is useful in batch control.

CONTROL OF THE SETTING TIME

As previously noted, it is necessary to control the setting time. Theoretically, there are at least three methods by which such control can be effected.

1. The solubility of the hemihydrate can be increased or decreased. For example, if the solubility of the hemihydrate is increased, supersaturation of the calcium sulfate will be greater. The rate of crystalline deposition is thus increased.
2. The number of nuclei of crystallization can be increased or decreased. The greater the number of nuclei of crystallization, the faster the gypsum crystals form and the sooner the hardening of the mass will occur because of crystalline intermeshing.
3. If the rate of crystal growth can be increased or decreased, the setting time can be accelerated or retarded, respectively.

In practice, these methods have been incorporated into the commercial products available. Then the operator can vary the setting time within reason by the W:P ratio and mixing time.

Impurities. If the calcination is not complete so that gypsum particles remain, or if the manufacturer adds gypsum, the setting time will be shortened because of the increase in potential nuclei of crystallization. If orthorhombic anhydrite is present, the induction period will be increased; it will be decreased if hexagonal anhydrite is present.

Fineness. The finer the particle size of the hemihydrate, the faster the mix hardens, particularly if the product has been ground during manufacture. Not only is the rate of the solution of the hemihydrate increased but also the gypsum nuclei are more numerous and, therefore, a more rapid rate of crystallization occurs.

W:P Ratio. The more water that is used for mixing, the fewer nuclei there are per unit volume. Consequently, the setting time is prolonged. This effect is evidenced by the results presented in Table 9-1.

Mixing. Within practical limits, the longer and the more rapidly the plaster is mixed, the shorter is the setting time. Some gypsum crystals form immediately when the plaster or stone is brought into contact with the water. As the mixing begins, the formation of these crystals increases; at the same time the crystals are broken up by the mixing spatula and are distributed throughout the mixture,

TABLE 9-1. Effect of the Water:Powder (W:P) Ratio and the Mixing Time on the Setting Time of Plaster of Paris

W:P Ratio	Mixing Time (min)	Setting Time (min)
0.45	0.5	5.25
0.45	1.0	3.25
0.60	1.0	7.25
0.60	2.0	4.50
0.80	1.0	10.50
0.80	2.0	7.75
0.80	3.0	5.75

From Gibson CS, and Johnson RN: J Soc Chem Ind 51:25T, 1932.

with the resulting formation of more nuclei of crystallization. Thus, the setting time is decreased, as indicated in Table 9-1.

Temperature. Although the effect of temperature on the setting time is likely to be erratic and may vary from one plaster (or stone) to another, little change occurs between 0° C (32° F) and 50° C (120° F); but if the temperature of the plaster-water mixture exceeds approximately 50° C (120° F), a gradually increasing retardation occurs. As the temperature approaches 100° C (212° F), no reaction takes place. At the higher temperatures, reaction 2 is reversed, with the tendency for any gypsum crystals formed to be changed to the hemihydrate form.

Retarders and Accelerators. Probably the most effective and practical method for the control of the setting time is the addition of certain chemical modifiers to the mixture of plaster or dental stone. If the chemical added decreases the setting time, it is known as an *accelerator*; if it increases the setting time, it is known as a *retarder*.

Retarders generally act by forming an adsorbed layer on the hemihydrate to reduce its solubility and on the gypsum crystals present to inhibit growth. Organic materials, such as glue, gelatin, and some gums, behave in this manner. Another type of retarder consists of salts that form a layer of a calcium salt that is less soluble than is the sulfate. In small concentrations, many inorganic salts act as accelerators, but when the concentration is increased they can become retarders. Because the action of these chemical additions also affects other properties such as setting expansion, the behavior of accelerators and retarders is discussed at greater length in a subsequent section.

SETTING EXPANSION

Regardless of the type of gypsum product employed, an expansion of the mass can be detected during the change from the hemihydrate to the dihydrate. Depending on the composition of the gypsum product, this observed linear expansion may be as low as 0.06% to as high as 0.5%.

On the other hand, if equivalent volumes of the hemihydrate, water, and the reaction product (dihydrate) are compared, the volume of the dihydrate formed will be less than the equivalent volumes of the hemihydrate and water. The calculations are as follows:

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(3)	$(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O} \longrightarrow 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$		
Molecular mass	290.284	54.048	344.332
Density (g/cm ³)	2.75	0.997	2.32
Equivalent volume	105.556	54.211	148.405
Total volume	159.767		
	148.405		

$$(4) \quad \text{Change in volume} = \left(\frac{148.405 - 159.767}{159.767} \right) 100 = -7.11\%$$

This represents a linear change in the gypsum object of -2.37%. Thus, according to these calculations, a volumetric contraction should occur during the setting reaction. However, a setting expansion is actually observed, and this phenomenon can be rationalized on the basis of the crystallization mechanism.

As previously noted, the crystallization process is pictured as an outgrowth of crystals from nuclei of crystallization. On the basis of the entanglement of the dihydrate crystals, as indicated in Figure 9-5, one can see that crystals growing from the nuclei can intermesh with and obstruct the growth of adjacent crystals.

If this process is repeated by thousands of the crystals during growth, an outward stress or thrust develops that produces an expansion of the entire mass. Thus, a setting expansion can take place even though the *true volume* of the crystals alone may be less as calculated. This crystal impingement and movement result in the production of micropores.

Because the product of the setting reaction for gypsum (reaction 2) in practice is greater in external volume but less in *crystalline* volume, it follows that the set material must be porous.

The structure immediately after setting is, therefore, composed of interlocking crystals, between which are micropores and pores containing the excess water required for mixing, as previously described. On drying, the excess water is lost, and the void space is increased.

As far as the technician or dentist is concerned, only the setting expansion that occurs after the initial set is of interest. Any expansion or contraction that occurs before this time can be overcome by friction between the mold surface onto which the plaster is poured and the fluid plaster. At the time of initial set, the crystalline framework is sufficiently rigid that it can overcome, for the most part, such frictional retention. However, it cannot always overcome any confinement by the mold boundaries. Furthermore, any initial contraction that occurs during the induction period does not affect the accuracy, because the mix is fluid at this stage and the contraction occurs at the free surface.

If a mixture of plaster and water is spread on a glass surface, the distance between any two surface reference points will not change appreciably during the induction period. The adhesion of the water-powder mix to the glass can prevent the linear contraction that is theoretically expected. Only when the crystalline framework is sufficiently rigid (after the initial set) is a visible setting expansion evident.

On the other hand, if the frictional factor is reduced by spreading the mixture on a frictionless surface such as liquid mercury, for example, the setting expansion curve shown in Figure 9-8 might result. The initial contraction is evident. When sufficient crystals form to produce the outward thrust by impingement, the setting expansion follows. The initial setting time occurs approximately at the minimal point of the curve, the point at which the expansion begins. According to

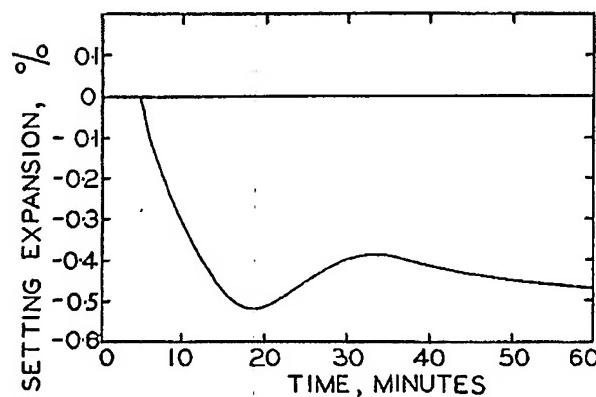


Figure 9-8. Dimensional changes that occur during the setting of a gypsum product. (Courtesy of A. R. Docking.)

the graph, the stone actually has shrunk during setting and it has not recovered its original dimensions. On the other hand, in the previous experiment on the glass plate, a setting expansion of approximately 0.12% would have been reported.

Control of Setting Expansion. As discussed in subsequent chapters, sometimes a setting expansion is advantageous in a dental operation and sometimes it is disadvantageous, because it may be a source of error. Consequently, it is necessary to control it to obtain the desired accuracy in dental applications.

As can be noted from the results presented in Table 9-2, the less the W:P ratio and the longer the mixing time within practical limits, the greater is the setting expansion. The effect of the W:P ratio on the setting expansion is to be expected on theoretical grounds. With the higher W:P ratios, fewer nuclei of crystallization per unit volume are present than with the thicker mixes, and because it can be assumed that the space between the nuclei is greater in such a case, it follows that there is less growth interaction of the dihydrate crystals and less outward thrust. However, the most effective method for the control of the setting expansion is the addition of chemicals.

ACCELERATORS AND RETARDERS: PRACTICE AND THEORY

Why are accelerators and retarders used? In industry, the gypsum product requires a gradual set or hardening so that the object may be formed or shaped over time. However, its use in dentistry generally involves pouring or vibrating the mix into a mold with any shaping requiring only a few minutes. At that

TABLE 9-2. Effect of the Water:Powder (W:P) Ratio and Mixing Time on the Setting Expansion of Plaster of Paris

W:P	Mixing Time (min)	Setting Expansion (per cent)
0.45	0.6	0.41
0.45	1.0	0.51
0.60	1.0	0.29
0.60	2.0	0.41
0.80	1.0	0.24

From Gibson CS, and Johnson RN: J Soc Chem Ind 51:25T, 1932.

time, the material should harden rapidly and will be ready for use within 30 minutes or less.

Figure 9-9 illustrates in a practical way the need for, and the interplay of, accelerators and retarders on the strength (in MPa units) of plaster. The same effects hold true for other gypsum products, including investments. The curve at the right shows the rate of hardening of a natural plaster, that is, a pure β -hemihydrate. It has only a few minutes of working time and then hardens gradually, usually too slowly for dental use. The addition of an accelerator (the curve at the left) produces a set that makes it possible to use the plaster within 30 minutes. However, the working time has been seriously reduced. Therefore, to make a usable plaster, it is necessary to also add a retarder (the curve in the middle). This increases the latent initial setting period so that the mix retains a reasonable plastic state that permits handling or working it into a useful shape. Then the mass hardens in time for use.

Not only do the chemical accelerators and retarders regulate the setting time of the gypsum products but also they generally reduce the setting expansion. The theory of such effects is still obscure.

Accelerators. Because the rate of setting is influenced by the rate of solution of the hemihydrate, it is logical to assume that materials that increase the rate of solution accelerate the reaction. However, it must be remembered that the rate of precipitation of the dihydrate is also important. Therefore, the accelerator must increase the solubility of the hemihydrate without also increasing the solubility of the dihydrate. Thus, the acceleration caused by an additive depends on the amount and rate of solubility of the hemihydrate versus the same effect on the dihydrate.

To further complicate matters, although inorganic salts are often accelerators, they can also become retarders when more than a certain amount is added. Sodium chloride is an accelerator up to about 2% of the hemihydrate, but at a

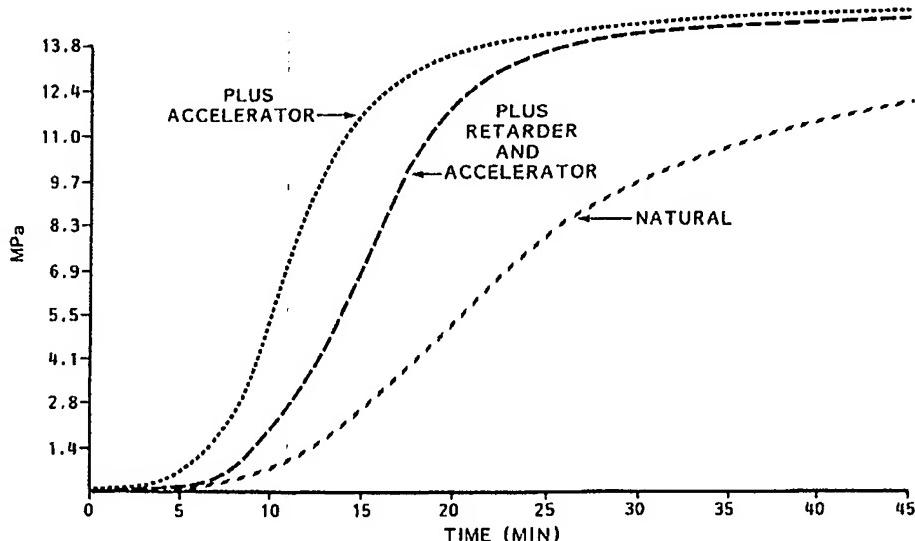


Figure 9-9. Compressive strength of a model plaster plotted against time when accelerators and retarders are added to the plaster. The gain in strength is a measure of the rate of hardening or setting.

higher concentration, it acts as a retarder. Sodium sulfate has its maximum acceleration effect at approximately 3.4%; at greater concentrations, it becomes a retarder.

The most commonly used accelerator is potassium sulfate. It is particularly effective in concentrations higher than 2%, since the reaction product, which seems to be syngenite ($K_2Ca[SO_4]_2 \cdot H_2O$), crystallizes rapidly. Many soluble sulfates act as accelerators, whereas powdered gypsum (calcium sulfate dihydrate) accelerates the setting, because the particles act as nuclei of crystallization. A slurry of ground gypsum casts acts in this way, although the clear saturated liquid is hardly effective. It takes the crystals themselves to accelerate the setting. Another way of accomplishing this effect is to increase either or both the time and the speed of mixing, because they increase the formation of more nuclei and thus accelerates the mix. Decreasing the mixing time or adding more water slightly retards the mix.

Retarders. The behavior of retarders is even more complicated. The common belief is that certain chemicals form a coating on the hemihydrate particles and thus prevent the hemihydrate from going into solution in the normal manner.

The citrates, acetates, and borates generally retard the reaction. For a given anion, the particular cation employed appears to affect the retardation markedly. For example, with the acetates, the order of retardation in terms of the cation employed appears to be $Ca^+ < K^+ < H^+$, whereas potassium tartrate has a marked accelerating effect in contrast with the calcium salt, which has little effect on setting. The behavior of citrates is more complex.

Because the manufacturer has already added accelerators and retarders and other control agents, it is not wise to add other ingredients as they may counteract the effects already incorporated into the product.

HYGROSCOPIC SETTING EXPANSION

It has been assumed in the discussion thus far that the plaster or stone is allowed to set in air. If the setting process is allowed to occur under water, the setting expansion may be more than doubled in magnitude. The reason for the increased expansion when the hemihydrate is allowed to react under water is related to the additional crystal growth permitted and not to any differences in chemical reaction 2.

The theory is illustrated diagrammatically in Figure 9-10. In Stage I, shown at the top of the figure, the initial mix is represented by the three round particles of hemihydrate surrounded by water.

In Stage II, the reaction has started and the crystals of the dihydrate are beginning to form. In the diagram on the left, the water around the particles is reduced by the hydration and the particles are drawn more closely together by the surface tension action of the water. In the right diagram, because the setting is taking place under water, the water of hydration is replaced and the distance between the particles remains the same.

As the crystals of dihydrate grow, they contact each other, and the setting expansion begins. As indicated in Stage III, the water around the particles is again decreased in the example on the left. The particles with their attached crystals tend to be drawn together as before, but the contraction is opposed by the outward thrust of the growing crystals. On the other hand, the crystals in the right diagram are not so inhibited, because the water is again replenished

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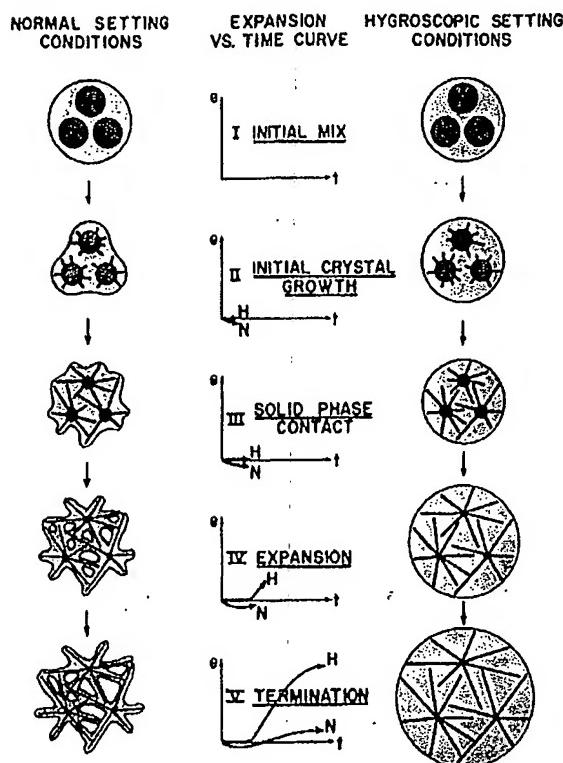


Figure 9-10. Diagrammatic representation of the setting expansion of plaster. In the left column, the crystal growth is inhibited by the lack of excess water. As shown in the right column, water added during setting provides more room for longer crystal growth. θ , expansion; t , time; H, hygroscopic setting expansion; N, normal setting expansion. (From Mahler DB, and Ady AB: Explanation for the hygroscopic setting expansion of dental gypsum products. J Dent Res 39:578, 1960.)

from the outside. In fact, the original particles are now separated further as the crystals grow, and the setting expansion is definitely evident.

In Stages IV and V, the effect becomes more marked. The crystals being inhibited on the left become intermeshed and entangled much sooner than those on the right, which grow much more freely during the early stages before the intermeshing finally prevents further expansion. Consequently, the observed setting expansion that occurs when the gypsum product sets under water may be greater than that which occurs during the setting in air.

It follows, therefore, that the basic mechanism of crystal growth is the same in both instances, and both phenomena are true setting expansions. To distinguish between them, the setting expansion without water immersion is often termed the *normal setting expansion* (N in Fig. 9-10), whereas the expansion that occurs under water is known as *hygroscopic setting expansion* (H in Fig. 9-10). The hygroscopic setting expansion is physical and is not caused by a chemical reaction any more than is the *normal setting expansion*. The reduction in the W:P ratio increases the hygroscopic setting expansion and the normal setting expansion in the same manner. Increased spatulation results in increased hygroscopic expansion as well.

The hygroscopic expansion obtained during the setting of dental stone or plaster is generally small in magnitude. For example, a dental stone used in making casts may exhibit a normal linear setting expansion of 0.15%, with a maximum hygroscopic expansion of not more than 0.30%. Nevertheless, this difference may be sufficient to cause the misfit of a denture or similar device made on the cast.

On the other hand, as explained in a subsequent chapter, the greater hygroscopic setting expansion of gypsum-bonded investments is sometimes used in the fabrication of cast restorations.

STRENGTH

The strength of gypsum products is generally expressed in terms of compressive strength, although tensile strength should also be considered if one is to secure a satisfactory guide to the total strength characteristics.

As might be expected from the theory of setting, the strength of a plaster or stone increases rapidly as the material hardens after the initial setting time. However, the free water content of the set product definitely affects its strength. For this reason, two strengths of the gypsum product are recognized: the *wet strength* (also known as *green strength*) and the *dry strength*. The wet strength is the strength obtained when the water in excess of that required for the hydration of the hemihydrate is left in that test specimen. When the specimen has been dried of the excess water, the strength obtained is the dry strength. The dry strength may be two or more times the wet strength. Consequently, the distinction between the two is of considerable importance.

The effect of drying on the compressive strength of set plaster is shown in Table 9-3. Note the relatively slight gains in strength that occurred after 16 hours. Between an 8-hour and 24-hour period, only 0.6% of the excess water was lost, yet the strength doubled. A somewhat similar change in surface hardness takes place during the drying process.

A good explanation of this effect is the fact that as the last traces of water leave, fine crystals of gypsum precipitate. These anchor the larger crystals. Then if water is added, or if excess water is present, these small crystals are the first to dissolve, and thus the reinforcing anchors are lost.

As previously noted, the set plaster or stone is porous in nature, and the greater the W:P ratio, the greater will be the porosity. As might be expected on such a basis, the greater the W:P ratio, the less is the dry strength of the set material, as shown by the data in Table 9-4, because the greater the porosity, the fewer crystals are available per unit volume for a given weight of hemihydrate.

The tensile strength of plaster or stone is less affected by variations in the W:P ratio than is the compressive strength. However, the materials mixed at a high W:P ratio have tensile strengths as high as 25% of the corresponding compressive strength. When materials are mixed at low W:P ratios, the tensile strength is less than 10% of the corresponding compressive strength.

As shown in Table 9-4, the spatulation time also affects the strength of the

TABLE 9-3. Effect of Drying on the Strength of Plaster of Paris

Drying Period (h)	Compressive Strength		Loss in Weight (per cent)
	MPa	psi	
2	9.6	1400	5.1
4	11.7	1700	11.9
8	11.7	1700	17.4
16	13.0	1900	—
24	23.3	3400	18.0
48	23.3	3400	18.0
72	23.3	3400	—

From Gibson CS, and Johnson RN: J Soc Chem Ind 51:25T, 1932.

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TABLE 9-4. Effect of the Water:Powder (W:P) Ratio and Mixing Time on the Strength of Plaster of Paris

W:P	Mixing Time (min)	Compressive Strength (Dry)	
		MPa	psi
0.45	0.5	23.4	3400
0.45	1.0	26.2	3800
0.60	1.0	17.9	2600
0.60	2.0	13.8	2000
0.80	1.0	11.0	1600

From Gibson CS, and Johnson, RN: J Soc Chem Ind 51:25T, 1932.

plaster. In general, with an increase in mixing time, the strength is increased to a limit that is approximately equivalent to that of a normal hand mixing for 1 minute. If the mixture is overmixed, the gypsum crystals formed are broken up, and less crystalline interlocking results in the final product.

The incorporation of an accelerator or retarder lowers both the wet and the dry strengths of the gypsum product. Such a decrease in strength can be partially attributed to the salt added as an adulterant and to the reduction in intercrystalline cohesion.

When relatively pure raw hemihydrate is mixed with minimal amounts of water, the working time is short and the setting expansion is unduly high. However, as just noted, dental gypsum products contain additives that reduce the setting expansion, increase the working time, and provide a rapid final set. The addition of more chemicals can upset the delicate balance of these properties. Thus, if a change is desired in the setting time it should be done by modest alterations in either or both the W:P ratio and the spatulation time.

TYPES OF GYPSUM PRODUCTS

Having discussed the basic principles of gypsum products, we turn our attention to the various types of dental gypsum and practical considerations in their use.

The criteria for selection of any particular gypsum product depend on its use and the physical properties necessary for that particular use. For example, a dental stone is a poor material for use as an impression material because if teeth are present it is impossible to remove the impression over the undercuts in the teeth without injury, because of the high strength of the stone (α -hemihydrate).

On the other hand, if a strong cast is required on which to build a denture, one would not choose to employ a weak plaster (β -hemihydrate). In other words, there is no all-purpose dental gypsum product.

The various types of gypsum products can be seen in Table 9-5. Listed are the five types identified by ADA Specification No. 25, and the properties required for each.

Impression Plaster (Type I). These impression materials are composed of plaster of Paris to which modifiers have been added to regulate the setting time and the setting expansion. Impression plaster is rarely used anymore for dental impressions, because it has been replaced by less rigid materials such as the hydrocolloids and elastomers (discussed earlier in Chapters 6 and 7). Plaster is primarily restricted to a final, or *wash*, impression in the construction of full dentures.

TABLE 9-5. Types of Gypsum Products*

Type	Fineness				Setting Expansion at 2 Hours		Compressive Strength at 1 Hour§	
	Setting Time (min)	Passes Sieves		Min (%)	Max (%)	kg/cm ²	psi	W:P Ratio
		150 μm (%)	75 μm (%)					
I. Plaster, impression	4 \pm 1	98	85	0.00	0.15	40 \pm 20	580 \pm 290	0.50-0.75
II. Plaster, model	12 \pm 4	98	90	0.00	0.30	90	1300	0.45-0.50
III. Dental stone†	12 \pm 4	98	90	0.00	0.20	210	3000	0.28-0.30
IV. Dental stone‡, high strength	12 \pm 4	98	90	0.00	0.10	350	5000	0.22-0.24
V. Dental stone, high strength, high expansion	12 \pm 4	98	90	0.10	0.30	490	7000	0.18-0.22

*Properties required in the 5 gypsum products covered by American Dental Association Specification No. 25. Typical water:powder (W:P) ratios are added at the right, and the traditional terminology for Types III and IV is seen at the bottom.

†III Dental stone, sometimes designated as Class I stone or Hydrocal.

‡IV Dental stone, high strength, sometimes designated as Class II stone, dentile, or improved stone.

§Minimum values.

Model Plaster (Type II). This model plaster or laboratory Type II plaster is now used principally to fill a flask in denture construction when setting expansion is not critical and the strength is adequate, according to the limits cited in the specification. It is usually marketed in the natural white color, thus contrasting with stones that are generally colored.

Dental Stone (Type III). In 1930 a major milestone was established when α -gypsum was discovered and introduced within dentistry. Combined with the advent of hydrocolloid impression material, the improved hardness of α -gypsum made stone dies workable and the indirect pattern became possible.

Dentistry shared in the greatest improvement in plaster that has been made in all of history. A researcher at U.S. Gypsum Corporation learned that the plaster mold used for forming rubber denture bases in a vulcanizer under steam pressure became unusually hard overnight. Examination showed that the set gypsum, calcined under steam pressure, formed a much better quality of crystallized calcium sulfate hemihydrate. Because of this improvement, it was soon thereafter patented as α -gypsum. Since this discovery, this process has been performed commercially in an autoclave.

Type III stone has a minimum 1-hour compressive strength of 20.7 MPa (3000 psi), but it does not exceed 34.5 MPa (5000 psi). It is intended for construction of casts in the fabrication of full dentures that fit soft tissues. Stone dies are reproductions of prepared teeth on or within which prostheses are constructed. Because of the severe wear conditions that occur at the margins during carving of wax patterns and because of the higher stresses induced in stone dies during try-in and adjustments, greater strength and hardness are required of die materials. This type of stone is discussed in the following sections. In addition, a slight setting expansion can be tolerated in casts that reproduce soft tissues but not when a tooth is involved. Type III stones are preferred for casts used to process dentures because the stone has adequate strength for that purpose and the denture is easier to remove after processing.

Regardless of the type of stone used, there are at least two methods for the construction of the cast. In one method, a mold for the cast is constructed by wrapping strips of soft wax around the impression so that they extend approximately 12 mm beyond the tissue side of the impression. A base for the cast is formed in this region. This process is called *boxing*. The mixture of stone and water is then poured into the impression under vibration. The mixture is allowed to flow slowly in a controlled pathway along the impression, so that it pushes the air ahead of itself as it fills all tooth impressions without entrapment of air bubbles.

Another method is to fill the impression first as described. The remainder of the stone-water mixture is poured on a glass plate. The filled impression is then inverted over the mound of stone, and the base is shaped with the spatula, before the stone sets. Such a procedure is not indicated if an impression material that is easily deformed has been used or if the stone is "runny." The cast should not be separated from the impression until it has initially hardened. The minimum time to be allowed for setting will vary from 30 to 60 minutes, depending on the rate of setting of the stone or plaster and the type of impression material used.

Dental Stone, High Strength (Type IV). The principal requisites for a die material stone are strength, hardness, and minimum setting expansion. To obtain these properties, an α -hemihydrate of the "Densite" type is used. The cuboidal-

shaped particles (Fig. 9-11) and the reduced surface area produce such properties without undue thickening of the mix. Summarized in Table 9-5 are some of the physical properties of Type IV stones compared with those of Type III stones.

A hard surface is necessary for a die stone, because the cavity preparation is filled with wax and carved flush with the margins of the die. A sharp instrument is used for this purpose; therefore, the stone must be resistant to abrasion. Gypsum hardening solutions and other methods of increasing the abrasion resistance are discussed in Chapter 23. It is fortunate that the surface hardness increases more rapidly than does the compressive strength, because the surface dries more rapidly. This is a real advantage in that the surface resists abrasion, whereas the core of the die is tough and less subject to accidental breakage. The average dry surface hardness of the Type IV stones ("die stones") is approximately 92 (Rockwell Hardness); that of Type III stone is 82. Even though the surface is harder, care should be observed when the pattern is being carved.

Dental Stone, High Strength, High Expansion (Type V). This is a recent gypsum product, having an even higher compressive strength than the Type IV dental stone. The improved strength is attained by making it possible to lower the W:P ratio even further. In addition, the setting expansion has been increased from a maximum of 0.10% to 0.30% (see Table 9-5). The rationale for the increase in setting expansion limits is that certain newer alloys, such as base metal, have a greater casting shrinkage than do the traditional noble metal alloys. Thus, higher expansion is required in the stone used for the die to aid in compensating for the alloy solidification shrinkage. Additional information on the use of Type IV and V stones is provided in the discussion of die materials in Chapter 23.

Synthetic Gypsum. It is also possible to make the α -hemihydrates and β -hemihydrates from the by-products or waste products of the manufacture of phosphoric acid. The synthetic product is usually much more expensive than that made from natural gypsum, but when the product is properly made, its



Figure 9-11. Powder particles of Type IV and V stones. $\times 400$.
(Courtesy of B. Giannara and R. Neiman.)

properties of some of the II stones. Preparation is instrument of abrasion. The abrasion of hardness of the surface of abrasion, leakage. The is approximately though the carved.

ent gypsum of IV dental over the W:P based from a increase in metal, have a thus, higher ensating for of Type IV ter 23.

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properties are equal to or exceed those of the latter. The processing problems are considerable, and few have succeeded. The methods employed are trade secrets, and no further discussion is appropriate. For our purpose, the source of the hemihydrate is not as important as the nature and use of the final product, which is essentially the same regardless of the origin.

PROPORTIONING, MIXING, AND CARING FOR PRODUCTS

Proportioning. Because the strength of a stone is indirectly proportional to the W:P ratio, it is most important to keep the amount of water as low as possible. However, it should not be so low that the mix will not flow into every detail of the impression. Once the optimum W:P is determined, using the manufacturer's suggested W:P as a guide, the same proportions should be adhered to subsequently. The water and powder should be measured by using an accurate graduated cylinder for the water volume and a weighing balance for the powder. The powder should not be measured by volume (use of a scoop), as it does not pack uniformly. It may vary from product to product and will pack harder as the container remains unused. If the container is shaken, then the volume will increase as a result of entrapment of air. Preweighed envelopes have become popular, because they promote accuracy, reduce waste, and save time.

Mixing. If mixing by hand, the bowl should be parabolic in shape, smooth, and resistant to abrasion. The spatula should have a stiff blade and handle that is convenient to hold. Entrapment of air in the mix must be avoided to avoid porosity leading to weak spots and surface inaccuracies, as illustrated in Figure 9-12. The use of an automatic vibrator, of high frequency and of low amplitude, is helpful. A measured amount of water is placed in the bowl, and the weighed powder is sifted in. The mixture is then vigorously stirred, with the periodic wiping of the inside of the bowl with the spatula to ensure the wetting of all of the powder and breaking up of any agglomerates, or lumps. The mixing should continue until a smooth mix is obtained, usually within a minute. A longer spatulation time drastically reduces the working time (see Table 9-1), particularly for pouring models.

The guesswork of repeatedly adding water and powder to achieve the proper consistency must be avoided. It yields an uneven set within the mass, resulting in low strength and distortion, one of the main causes of inaccuracy in the use of gypsum products.

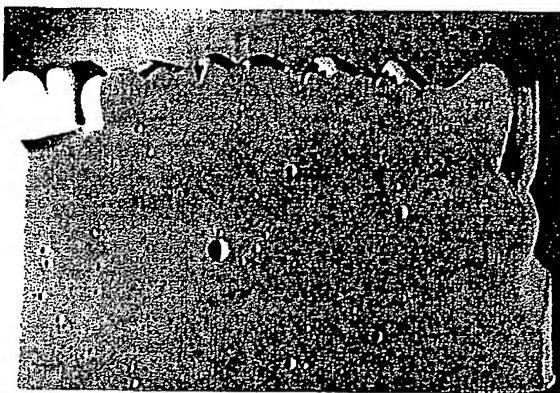


Figure 9-12. Section through a cast of a set stone that was improperly mixed. Air voids weaken the stone and impair its appearance.

The preferred method of mixing is to add the measured water first, followed by gradual addition of the preweighed powder. The powder is incorporated during approximately 15 seconds of mixing with a hand spatula, followed by 20 to 30 seconds of mechanical mixing under vacuum by a mixer. In this way, a properly mixed stone results in a solid cast (Fig. 9-13). The strength and hardness obtained in such mechanical vacuum mixing usually exceed that obtained by 1 minute of hand mixing.

Caring for the Cast. If the surface of the cast is not hard and smooth when it is removed from the impression, its accuracy is questionable. The cast is supposedly an accurate reproduction of the oral tissues, and any departure from the expected accuracy will probably result in a poorly fitting prosthesis. The cast should, therefore, be handled carefully. Once the setting reactions in the cast have been completed, its dimensions will be relatively constant thereafter under ordinary conditions of room temperature and humidity. As later outlined, however, it is sometimes necessary to soak the gypsum cast in water, in preparation for other techniques. The gypsum of which the cast is composed is slightly soluble in water. When a dry cast is immersed in water, there may be a negligible expansion, provided that the water is saturated with calcium sulfate. If it is not so saturated, gypsum may be dissolved. If the stone cast is immersed in running water, its linear dimension may decrease approximately 0.1% for every 20 minutes of such immersion. The safest method for soaking the cast is to place it in a water bath made for the purpose, in which plaster debris is allowed to remain constantly on the bottom of the container to provide a saturated solution of calcium sulfate.

As previously noted, storage of either set plaster or stone at room temperature produces no significant dimensional change. However, if the storage temperature is raised to between 90° and 110° C (194° to 230° F), a shrinkage occurs as the water of crystallization is removed and the dihydrate reverts to the hemihydrate. The contraction of the plaster at high temperature is greater than that of the stone, and it also loses strength.

Such contractions may occur during storage in air above room temperature, as when a stone cast is dried. Probably it is not safe to store or heat a stone cast in air at a temperature higher than 55° C (130° F).

Special Gypsum Products. In addition to the standardized gypsum materials just described, there are some that have been characterized for special purposes. For example, the orthodontist prefers a white stone or plaster for study models

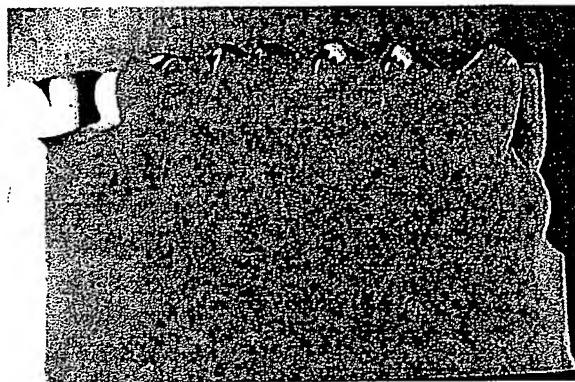


Figure 9-13. Section through a cast of a set stone that was properly proportioned and mixed.

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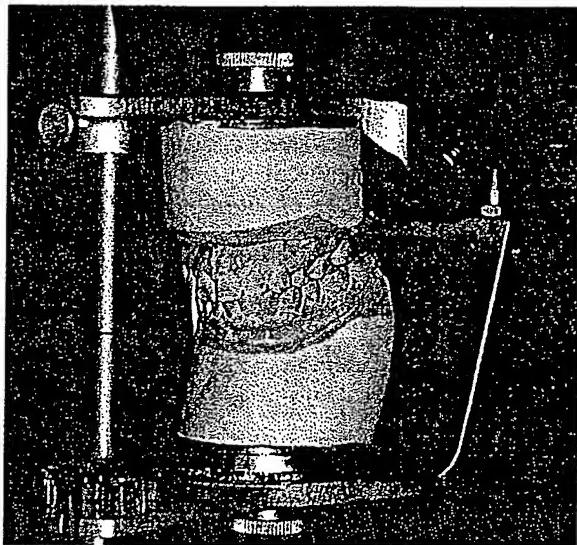


Figure 9-14. Dental articulator, a device that incorporates artificial temporomandibular joints. This permits orientation of casts in a manner that simulates various positions of the mandible. (Courtesy of C. Munoz.)

and may even treat the surface with soap for an added sheen. These products generally have a longer working time for ease of trimming.

The use of an articulator makes it necessary to mount the casts with a gypsum product, as shown in Figure 9-14. These materials are referred to as "mounting" stones or plasters. They are fast setting and have low setting expansion. In the case of the mounting plaster, it has low strength to permit easy trimming and to separate the cast readily from the articulator mounting plates.

Since 1991, a plethora of new dental stones have appeared, mostly as time savers. One type is extremely fast setting and ready to use in 5 minutes, but it has little working time. Another product changes color to help denote when it is ready for use. Most recently, the trend is to add a small amount of plastic or resin that reduces the brittleness and improves the resistance to scratching during the carving of wax patterns.

Usually, when one feature is improved, another feature is sacrificed. A faster set is accepted in return for less working time. An improved resistance to carving is accepted in return for a greater difficulty in incorporation, the need to box the impression because of excessive runniness, and decreased detail reproduction. Improvements in materials and testing equipment have made it possible to use silicone-stone combinations that can reproduce spacings between lines as fine as 10 μm or less. Current specifications require an accuracy of only 50 μm .

Currently, there is a wide choice of gypsum products available to suit almost any desired individual requirements or combinations thereof.

Caring for Gypsum Products. Gypsum products are somewhat sensitive to changes in the relative humidity of their environment. Even the surface hardness of plaster and stone casts may fluctuate slightly with the relative humidity of the atmosphere. Gypsum surfaces made with thinner mixes appear to be affected more than those with a low W:P ratio.

The hemihydrate of gypsum takes up water from the air readily. For example, if the relative humidity exceeds 70%, the plaster takes up sufficient water vapor to start a setting reaction. The first hydration probably produces a few crystals of gypsum on the surface of the hemihydrate crystal. These crystals act as nuclei

of crystallization, and the first manifestation of the plaster deterioration is a decrease in the setting time.

As the hygroscopic action continues, more crystals of gypsum form until the entire hemihydrate crystal is covered. Under these conditions, the water penetrates the dihydrate coating with difficulty, and the setting time is unduly prolonged. It is, therefore, important that all types of gypsum products be stored in a dry atmosphere. The best means of storage is to seal the product in a moisture-proof metal container. When gypsum products are stored in closed containers, generally the setting time is retarded only slightly, approximately 1 or 2 minutes per year. This may be counteracted by a slight increase in the mixing time if necessary.

INFECTION CONTROL CONCERNs

As noted elsewhere in this text, there is increased interest in expanding infection control measures to the dental laboratory. Concern over possible cross-contamination to dental office personnel by micro-organisms, including hepatitis B virus and human immunodeficiency virus, via dental impressions has prompted study of the effect of spray and immersion disinfecting techniques on impression materials, as discussed in Chapter 7. The effect of such agents on the surface quality and accuracy of the resulting gypsum casts is an important consideration.

If an impression were not disinfected, or if the laboratory has no assurance that an appropriate disinfection protocol was followed, it is prudent to disinfect the stone cast. Disinfecting solutions can be used that do not adversely affect the quality of the gypsum cast. Alternatively, a dental stone containing a disinfectant may also be employed. Although the addition of a disinfectant may have a slight effect on some of the physical properties of certain products, the disinfected stones apparently compare favorably with the nondisinfected controls.

The widespread availability of a spectrum of disinfecting dental stones (Types II to V) with proven efficacy and unimpaired physical properties would undoubtedly strengthen the barrier system of infection control in the dental laboratory. When patients with known cases of infection are being treated, overnight gas sterilization is an option. However, the procedure is impractical for routine use by practitioners and dental laboratory personnel.

In the United States, the incorporation of disinfectants in dental stones has been delayed by failure to obtain approval of the U.S. Food and Drug Administration.

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Gypsum

PHYSICAL PROPERTIES OF CALCINED GYPSUM

Theoretical work on the system $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ involving specific heat measurements, heat of hydration, thermodynamic data, dissociation-equilibrium measurements and stability diagrams reviewed in terms of practical calcining

TECHNICAL PAPER No. 626, U. S. Bureau of Mines, published by Kelsey, Southard and Anderson in 1941 is a critical study of gypsum and its dehydration products. This theoretical study covered a period of about two years and the following subjects are discussed in detail:

1. The various forms of calcium sulfate and its hydrates and their preparation.
2. Heats of hydration.
3. Specific heats.
4. Dissociation-equilibrium measurements.
5. Correlation of thermodynamic properties.
6. Stability diagrams of system $\text{CaSO}_4 \cdot \text{H}_2\text{O}$.

This work is the most complete and careful study of the system $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ since J. H. van't Hoff published his studies of gypsum in 1901.

This article is an attempt to review, if possible, in more readily usable form the theoretical data in Technical Paper 626. Additional data also are presented and the authors of Technical Paper 626 should not be held accountable for any of the statements made here. Southard discusses and reviews the published data on the various forms of calcium sulfate and hydrates and concludes:

All the varieties of the dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ have the same energy content and probably the same crystalline form: monoclinic prismatic, with 4 or 8 molecules in the unit cell. From x-ray diffraction studies the crystal lattice is considered made up of layers of calcium atoms and sulfate groups separated by sheets of water molecules. It should be noted that the water molecules occupy a special position in the crystal lattice and that it should be impossible to remove any of the combined water without destroying the lattice, and therefore any lower hydrate of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ should have a different structure than that of the dihydrate; in fact, all the dehydration products of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ give x-ray powder photographs dia-

By W. C. RIDDELL*

Distinctly different from that of gypsum. This important position of the water molecules in the gypsum lattice, and the difference in structure of its dissociation products, could well account for the period of induction which can be readily observed when pure gypsum is dehydrated.

Dehydration Curves

In Fig. 1, a dehydration curve of Plaster City rock gypsum clearly shows the induction period. Similar dehydration curves have been plotted for gypsum samples from many localities and the effect of inorganic and organic compounds on the temperature and rate of dehydration has been studied. Fig. 2 shows typical examples of dehydration curves for gypsum in the presence of 0.1 to 0.2 percent of several salts. Similar curves have been plotted for many of the soluble sulfates, chlorides, nitrates, hydroxides, phosphates and a number of solu-

ble organic compounds as well as dehydration curves in partial vacuum. A trace of most soluble salts affects the decomposition temperature of gypsum, and this is one of the methods of determining their presence.

The difference in structure between the dihydrate and hydrates of lower water content would also seem evident from the fact that a few lb. per ton of ground gypsum or pre-set plaster $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ added to calcined gypsum, which is essentially $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, will materially accelerate the setting time. If both of these materials had the same crystalline structure, no effect on setting time should be observed. Davis discusses this in his article on "Production and Setting of Plaster of Paris."

Forms of Hemihydrate

There are two forms of the hemihydrate, alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ and beta $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. It is the consensus of opinion that the hemihydrate, $\text{CaSO}_4 \cdot$

*W. A. Davis, Jour. Soc. Chem. Ind., Vol. 86 (1907)

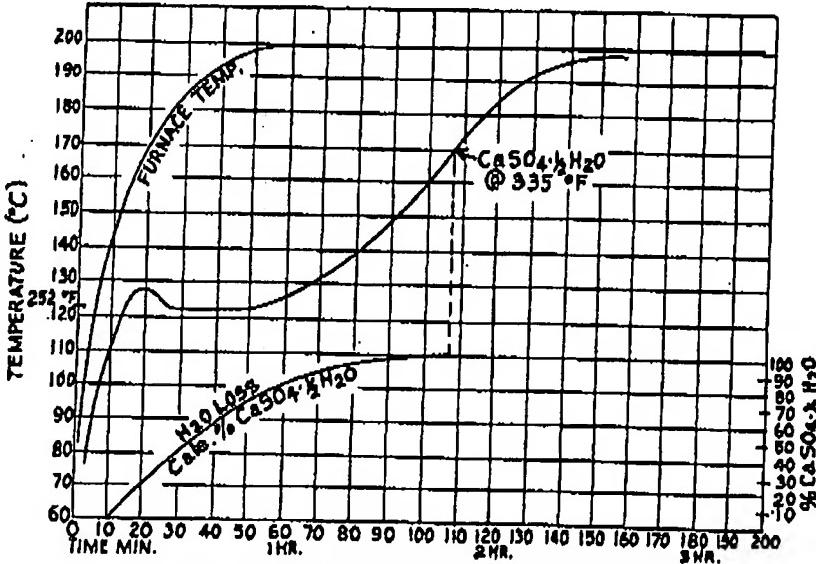


Fig. 1: Dehydration curve of Plaster City Rock Gypsum

*Chemical Engineer, Kaiser Gypsum Co., Oakland, Calif.

GYPSUM

$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ is the only lower hydrate of calcium sulfate, the identity of which has been established with any degree of certainty. Perhaps the most important work is that of Galliotti.^{1,2} He describes the hemihydrate as a deformed monoclinic structure with 12 molecules of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ in a unit cell, and says the lattice structure possesses great stability because the calcium atoms and sulfate tetrahedrons are so arranged that there are strong bonds between the calcium atoms in one layer and the sulfate groups of the adjacent ones, and that there are channels within the lattice in which the water molecules are situated. The forces holding the water molecules are less than the forces between the other groups and this permits at least part of the water to be removed without disrupting the crystalline structure. This effect is just the opposite of that which takes place in the case of removal of the water molecules in the dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

The recorded data agree well with this postulation; dissociation of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ to form $\text{CaSO}_4 + \text{H}_2\text{O}$ proceeds with no induction period until the major portion of the water is removed; x-ray investigations all agree that no noticeable change in structure can be detected.

Alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ can be prepared by dehydration of gypsum in water above a temperature of 97 deg. C., by dissociation in a salt solution below this temperature, and by dissociation in an atmosphere of steam.

Beta $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ can be prepared by dissociation of gypsum in a vacuum at 100 deg. C.

It should be noted that in the dehydration of gypsum to produce $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ by the "kettle process," in which steam is always present, alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ is always produced in greater or lesser amounts, depending on kettle construction, time of heating and temperatures. Exhaust fan from the kettle top, rapid heating of the kettle and rate of loading the kettle all affect the amount of alpha hemihydrate formed.

Both the alpha and beta form of hemihydrate have the same crystalline form; however, the beta form has a definitely higher energy content and a higher solubility. Southard determined the heat of hydration of samples of calcined gypsum made by the "kettle process" in a standard type 10 ft. dia. x 12 ft. deep Ehraam kettle. His results indicate that, in this particular kettle, the calcined hemihydrate produced for use as hardwall plaster had the composition of 75 percent alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ plus 25 percent beta $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, and that the hemihydrate made by the addition in the kettle of 0.1 percent of a salt, such as CaCl_2 , produced for the man-

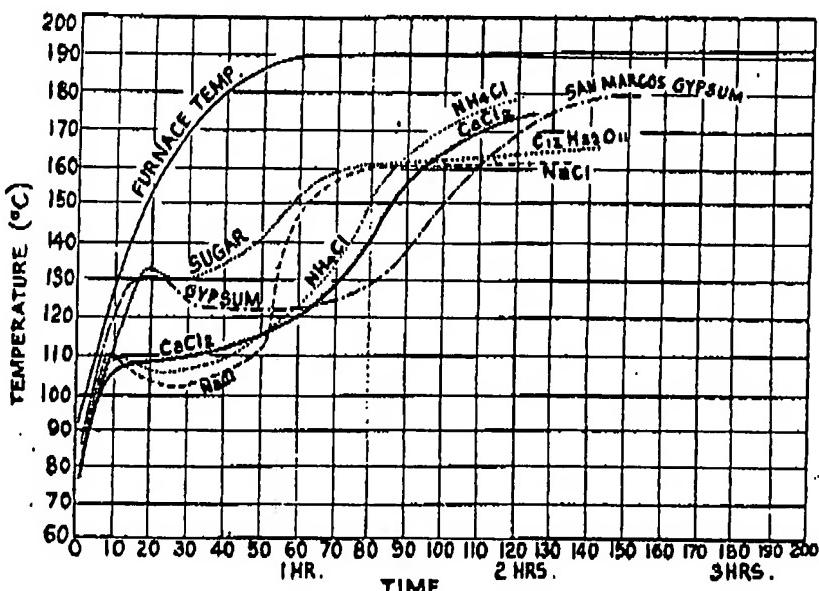


Fig. 2: Dehydration curves of gypsum plus 0.1 percent salts

facture of casting plasters, was practically all in the form of alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. This is probably the first authentic evidence we have that alpha hemihydrate is produced by the "kettle process" and that this product has the same physical structure as that of alpha hemihydrate produced by other process apparatus. Fig. 2 is typical of many curves plotted for the addition of various other salts in varying molar proportions which indicate a marked change in the dehydration of gypsum to hemihydrate.

Soluble Anhydrites

Tests on pure beta hemihydrate show an extremely high water-carrying capacity and normal consistency, comparable with that of lime putties; dehydration in the presence of certain salts will produce a hemihydrate of relatively low normal consistency. There are two forms of soluble anhydrite, CaSO_4 , corresponding to the alpha and beta forms of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. They have different heats of hydration and different solubility.

Alpha soluble anhydrite can be prepared by dehydration of alpha hemihydrate in a vacuum at 100 deg. C. or at 110 deg. C. in air saturated with water vapor at room temperature.

Beta soluble anhydrite can be prepared by dehydration of beta hemihydrate at 100 deg. C. or by heating gypsum in an atmosphere of low water vapor content at 140 to not over 200 deg. C.

Both forms of soluble anhydrite contain some residual water, alpha $\pm .05$ percent and the beta from 0.6 to 0.9 percent. It is virtually impossible to dehydrate completely the beta form without affecting its physical properties. Both forms are excellent drying reagents, absorbing water to form hemihydrate, and are largely used in

industry as such. They can be regenerated by heating to below 200 deg. C. or for short periods at as high as 250 deg. C.

It should be noted that both the alpha and beta hemihydrates absorb as much as 1 percent more water than is required for the formula $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. The amount of water held is dependent on temperature and humidity conditions and can be removed below 66 deg. C. in normal air. Plaster on storage tends to become "dead," that is, lean working, particularly when stored under conditions of high humidity. Alpha hemihydrate is the more stable form and heat of hydration measurements indicate that beta hemihydrate gradually changes to alpha hemihydrate when aged under humid conditions. This would account for the change taking place in the workability of plaster on storage.

Insoluble Anhydrite

There is only one form of insoluble or natural anhydrite, CaSO_4 . This can be prepared by heating gypsum or soluble anhydrites at 900 deg. C. for one hour. It can also be prepared by crystallization from salt solutions at about 100 deg. C.

Insoluble anhydrite does not take up water at any appreciable rate. It has the lowest solubility in water of any of the calcium sulfates. It is a simple orthorhombic lattice; the unit cell contains 4 molecules and the lattice has the maximum packing, highest density and most stable arrangement of any of the calcium sulfates. Natural and artificial anhydrites have the same optical and thermal properties.

The heats of hydration of calcium sulfates are summarized in Table I.

It is evident from these data that there is no difference in the energy

¹Galliotti, Periodico Mineral, Vol. 4 (1938)
²Galliotti, Nuova Journ. Mineral. Geol., Referate I, (1938)

GYPSUM

Form	Reaction	Calories per gram formula mass	B.t.u. per lb.	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
$\text{CaSO}_4 \cdot (\text{anhydrite}) + 2\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-4080	42.1		
$\text{CaSO}_4 \cdot (\beta\text{soluble anhydrite}) + 2\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-7210	76.4		
$\text{CaSO}_4 \cdot (\alpha\text{soluble anhydrite}) + 2\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-8160	84.4		
$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} \cdot (\text{hemihydrate}) + 1\frac{1}{2}\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-4100	42.9		
$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} \cdot (\text{hemihydrate}) + 1\frac{1}{2}\text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-4600	48.1		
Commercial hemihydrate $\text{Ca} \frac{1}{2} \text{alpha CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	-4230	44.9		
Average commercial hemihydrate $\frac{1}{2} \text{beta CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ estimated as	-4800	45.0		
Heat of solution in calories per gram formula mass of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in 58.48 kg. of 2.08 normal HCl at 25 deg. C. =				
Gericke selenite		5700		
Alaska rock gypsum		5698		
Set plaster (from San Marcos rock gypsum)		5682		
hemihydrate containing 20.92 percent H_2O		5708		
Precipitated $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$		5710		

Table I. Heats of hydration of calcium sulfates

content of various samples of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and that if any differences are observed they must be differences in mechanical condition and not in crystalline form.

Table I shows the heats of hydration of the definitely known calcium sulfates. Calories per gram formula mass are calculated to B.t.u. per lb. by dividing by 172 and multiplying by 1.8. It is estimated that in the production of commercial calcined gypsum, essentially $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, the average kettle with a calcining period of 2 to 2½ hours, the average heat of hydration would be 4800 cal. per 4800
 $\text{g.f.m.} \times \frac{1.8}{172} = 45.0 \text{ B.t.u. per lb.}$

or 90,000 B.t.u. per ton of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The average heat required per ton of gypsum feed, which also takes into consideration the heat carried off in the liberated water vapor and heat in the calcined product discharged at 340 deg. F. is calculated by the above process as 560,000 B.t.u. per ton of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Calculating an average loss of 15 percent combined water, this would give 550,000 + .85 = 647,000 B.t.u. per ton of calcined $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ produced.

Production figures for a 10-ft. dia. x 12-ft. deep Ehrsam kettle show that it requires an average of 8 gal. of oil (160,000 B.t.u./gal.) or 1,200,000 B.t.u. per ton of stucco produced. An approximate calculation gives $647,000 + 1,200,000 = 54$ percent as the practical furnace efficiency under existing operating conditions. It does not take into account the efficiency which might be attained if the available heat in the water vapor and the stack gases were utilized. Similar calculations on natural gas-fired kettles of the same size and construction show an average of 1025 cu. ft. of gas used (1140 B.t.u. per cu. ft. gross = 1,170,000 B.t.u.) per ton of calcined gypsum produced, and $647,000 + 1,170,000 = 55.8$ percent as the practical furnace efficiency.

Kelley computes the mean specific heat for the interval 84 deg. to 350

deg. F. as 0.220 B.t.u. per lb. for calcined gypsum (plaster) allowing for the relative proportions of alpha and beta $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ and soluble beta CaSO_4 formed in the kettle. This average figure of 0.220 B.t.u. per lb. of kettle-calcined gypsum can be used to advantage in calculating the heat

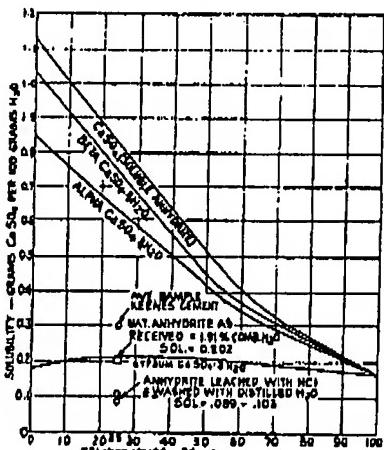


Fig. 2. Solubility curves of gypsum and CaSO_4 hydrates

loss in the calcined product. This figure times the weight of the calcined charge times the difference in temperature of the gypsum feed and the discharge test equals heat loss in B.t.u.

The dissociation-equilibrium measurements made by Southard show that different samples of gypsum have the same lattice energy, that there is only one crystalline form of gypsum, and

that alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ can be produced in liquid water at approximately 100 deg. C. and below in a water solution of lowered activity. In this case, Southard used alcohol, but a salt could be added to lower the activity of the water. Southard's data give 100 ± 1 deg. C. as the temperature at which $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ and water are in equilibrium. Partridge and White give the equilibrium temperature at between 98 and 100 deg. C.; Posnjak gives it as 97.5 ± 1 deg. C. at a temperature of 97 deg. C., as calculated from the free-energy equation.

We have made solubility determinations, over the range of 0 deg. to 100 deg. C. on $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, beta $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ soluble anhydrite and insoluble anhydrite. Fig. 2 gives this data, and it should be noted that the solubility curves of the lower hydrates intersect the solubility curve of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ between the temperature of 97 to 100 deg. C., which corresponds to the equilibrium temperature. The solubility data are given in Table III.

Solubility determinations have been made on samples of natural anhydrite from various deposits. All of these samples contained combined water varying from 1.6 to over 2 percent. Solubility determinations on a sample of natural anhydrite analyzing 1.91 percent combined H_2O gave .202 gram CaSO_4 per 100 cc. solution at 25 deg. C., which is equivalent to the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at this temperature.

Part of this sample was leached with HCl, washed with distilled water and dried at 60 deg. C. This sample was free from combined water and the solubility at 25 deg. C. was:
 In 16 min. = .0460 gm. CaSO_4 for 100 cc. sol.
 In 1 hr. = .0980 gm. CaSO_4 for 100 cc. sol.
 In 24 hr. = .1080 gm. CaSO_4 for 100 cc. sol.
 The average solubility of several samples of Keenes cement, as received, was .2982 grams CaSO_4 per 100 c.c. solution at 25 deg. C. The solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 25 deg. C. is .201 grams. Keenes cement with a lower solubility than .201 at 25 deg. C. will not set.

Samples of gypsum, analyzing 97 percent $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, were ground and calcined in a Raymond Imp mill at 310 deg. F. to fineness of 90 percent minus 200-mesh and combined H_2O content of 5.95 percent. Solubility determination at 20 deg. C. on these samples gave a solubility of .808

	Calculated in calories per gram formula mass	Calculated B.t.u. per lb.
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$C_p = 21.84 + .076 T$	@ 80 deg. F. = 0.259
$\alpha\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	$C_p = 18.95 + .039 T$	@ 340 deg. F. = 0.2363
$\beta\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	$C_p = 11.84 + .061 T$	@ 340 deg. F. = 0.266
CaSO_4 (all varieties)	$C_p = 14.10 + .088 T$	@ 340 deg. F. = 0.212
H_2O (gas)	$C_p = 7.45 + .002 T$	
H_2O (liquid)	$C_p = 18.02$	

Table II. Specific heats of the calcium sulfates (after Kelley)

GYPSUM

grams of CaSO_4 per 100 c.c. solution. From the solubility chart, which gives the solubility of beta $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ at 20 deg. C. as .802, it would appear that Imp mill material may be considered largely beta $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. This type of calcining apparatus should produce a high percentage of beta hemihydrate, as the mill temperatures are high and water vapor concentrations low and very rapid dehydration is accomplished. As shown by Kelley and Southard these conditions favor the formation of beta hemihydrate.

In the correlation of the thermodynamic properties of gypsum and its dehydration products, Kelley and Southard give the free energy equation for the formation of alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, beta $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ and the corresponding alpha and beta CaSO_4 (soluble anhydrites) and CaSO_4 (insoluble). Little would be gained by quoting here the equations and calculations of Kelley and Southard, as the original text can be consulted. However, certain data derived from these calculations are of practical interest:

"It appears that a rapid disruptive reaction is necessary in forming beta $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$." The temperature at which $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ and liquid water are in equilibrium is 97 deg. C.; this equilibrium temperature can be depressed by the presence of soluble salts or other substances that lower the activity of the water and alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ can be formed at as low a temperature as 26 deg. C. if the activity of H_2O is 0.38.

The reaction $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons$ beta soluble $\text{CaSO}_4 + 2\text{H}_2\text{O}$ occurs either directly or indirectly to some extent in the kettle manufacture of plaster or in a very rapid calcining of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

"Either variety of soluble CaSO_4 (alpha or beta), at ordinary temperatures is less stable than either variety of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$." At all temperatures below 191 deg. C., alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ is more stable than beta $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ and therefore at plaster making temperatures alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ should be obtained if the conditions are favorable for recrystallization. In the presence of liquid water pure alpha hemihydrate always forms and a slow dissociation in the presence of steam forms this product.

A summary of the more important heats of hydration of the calcium sulfates is shown in Table IV.

Hydrogen ion determinations on various samples of gypsum and plaster are shown in Table V. Determinations were made with saturated calomel-quinhydrone and antimony electrode assemblies at 20 deg. C. The results are shown therein.

The apparent acidity of calcined gypsum may account for certain reactions in the control of the setting time
(Continued on page 102)

Hulett and Allen data for solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$		Author's data for solubility of alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	
Temp. deg. C.	Grams CaSO_4 per 100 c.c. sol.	Temp. deg. C.	Grams CaSO_4 per 100 c.c. sol.
0	.1769	8	.825
10	.1928	11	.748-.750
20	.2090	21	.662
40	.2007	24	.648
50	.2038	31	.598
60	.1906	50	.426-.424
80	.1802	75	.270-.271
100	.1610	93	.104-.102

Author's data for solubility of beta $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$		Author's data for solubility of CaSO_4 (soluble anhydrite)	
Temp. deg. C.	Grams CaSO_4 per 100 c.c. sol.	Temp. deg. C.	Grams CaSO_4 per 100 c.c. sol.
0	1.034	2	1.15
3	1.006	3	1.18
4	.994	14	.060-.002
25	.744-.748	23	.854-.850
40	.578-.580	34	.710-.708
50	.460-.462	53	.482
65	.350	62	.308
75	.286-.284	64	.286
86	.228	77	.284
96	.180-.181	78	.278
		94	.188

Table III. Comparison of data for solubilities of calcium sulfate hydrates

Reaction	Heat of reaction $\Delta H_{E.I.M.}$	Calculated B.t.u./lb.
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4$, insoluble anhydrite + $2\text{H}_2\text{O}$ liquid	4080	42.2
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ alpha + $\frac{3}{2}\text{H}_2\text{O}$	4100	42.0
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ beta + $\frac{3}{2}\text{H}_2\text{O}$	4600	48.1
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4$, soluble anhydrite + $2\text{H}_2\text{O}$	6150	64.4
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4$, beta soluble anhydrite + $2\text{H}_2\text{O}$	7210	75.4
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ hardwall plaster + $\frac{3}{2}\text{H}_2\text{O}$	4280	44.3
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ casting plaster + $\frac{3}{2}\text{H}_2\text{O}$	4180	43.2
(Calculated B.t.u./lb. = gram formula mass + molecular weight \times 1.8; e.g., 4080		
$\rule{1cm}{0pt} \times 1.8 = 42.2$ B.t.u.).		
172		

Table IV. Important heats of hydration

Material	pH
San Marcos gypsum, Lower Calif.	7.8
Plaster City gypsum, Calif.	7.0
Gerlach gypsum, Calif.	7.8
Pure selenite from Gerlach, Calif.	7.0
Alabaster gypsum, Alaska	7.0
Anderson deposit, Gerlach, Nevada	6.1
Gypsum Clark Co., Nevada	7.7
Set dry gypsum (one year old)	7.0
Newark synthetic gypsum	6.6
Plasters:	
Alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (from Alaska gypsum)	5.10
Alpha $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (from U.S.B.M.)	5.35
Beta $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ (from U.S.B.M.)	4.85
Soluble anhydrite CaSO_4 (from U.S.B.M.)	4.80
Hardwall plaster stucco made in kettle, San Marcos rock	6.80
Hardwall plaster stucco made in kettle, Gerlach rock	6.60
Hardwall plaster stucco made in kettle, Plaster City rock	6.40
Casting plaster stucco made in kettle, Plaster City rock	6.60
Fibered hardwall plaster at 10 min.	11.60
Fibered hardwall plaster at 1 hr.	10.40
Fibered hardwall plaster at 24 hr.	7.00

Table V. Hydrogen ion determinations on various samples of gypsum and plaster

Gypsum

(Continued from page 71)

	Stable $\alpha\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	Metastable $\beta\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$
Normal consistency (c.c. $\text{H}_2\text{O}/100$ gm.)	85	90
Neat setting time (minutes)	15-20	25-35
Expansion	.0028	.0016
Specific gravity	2.757	2.637
Specific volume	52.65	55.05
Heat of hydration (calories gram formula mass)	4100	4000
Heat of hydration (B.t.u./lb.)	42.9	48.1
Specific heat (B.t.u./lb. @ 25 deg. C.)	.286	.266
pH at 20 deg. C.	5.85	4.85
Ave. tensile strength (1 hr. after set wet p.s.i.)	500	100
Ave. tensile strength (dry p.s.i.)	1000	200
Average compressive strength (1 hr. after set wet p.s.i.)	4000	400
Average compressive strength (dry p.s.i.)	8000	800
Solubility (grams CaSO_4 per 100 c.c. sol. @ 20 deg. C.)	0.63	0.74

Table VI. Physical properties of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$

of hardwall plasters. Commercial retarders generally are made from protein materials such as hair, horns and hoofs, etc., by treatment with sodium hydroxide to render them soluble in water. These soluble protein materials are extended with lime to make a commercially usable material. They are highly soluble in an alkaline solution and practically insoluble in a neutral solution. They are amphoteric and become insoluble at definite pH values. It is possible, in the setting reaction of hardwall plaster, that the acid properties of the calcined gypsum gradually neutralize the alkalinity of the retarder, rendering the protein compounds insoluble and thus no longer able to delay crystallization or set. Tests of sanded set hardwall plaster, after complete set has taken place, give a pH of 7.0. Approximately 7 lb. of retarder are added to hardwall plaster to control set. The probable maximum hydroxyl ion concentration in an average sample of hardwall plaster is calculated to be approximately 1.95 lb. and to neutralize this quantity of hydroxyl ion to produce a pH of 7.0—at which point the protein material in the retarder is insoluble and no longer active, would require 0.115 lb. of hydrogen ions. Samples of hardwall plaster have been tested in a Blaine permeability apparatus and the results indicate a surface area of 2000 to 3000 sq. cm. per gram. These calculations indicate a layer of hydrogen ions approximately one molecule thick on the surface of the calcined gypsum particles.

Applying the data previously recorded, the heat required to dehydrate gypsum and produce a commercial product, essentially $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, can be calculated with sufficient accuracy for all technical purposes as follows:

(a) Average heat required to decompose $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to kettle product essentially $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} = 45.0$ B.t.u. per lb. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in feed.

(b) Average heat required to raise

the temperature of calcined product from the feed temperature to kettle discharge temperature equals the specific heat \times weight of calcined product produced. (Average specific heat = 0.220.)

(c) Average heat required and carried off in the water vapor formed from the decomposition of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + 1 \frac{1}{2}\text{H}_2\text{O}$ (water vapor) equals $27/172 (= .157) \times$ percentage of gypsum in the feed \times average specific heat of the water vapor (.448) \times (average calcining temperature—atmospheric temperature).

For gypsum analyzing 96 percent $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $a + b + c = 550,000$ B.t.u. per ton of feed. For a kettle using 7 gal. of oil (148,000 B.t.u. per gal.) per ton of feed, heat supplied to kettle = $7 \times 148,000 = 1,036,000$ B.t.u. and the practical furnace efficiency = $1,036,000/550,000 = 53.1$ percent. The general average physical properties of essentially pure $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ are summarized in Table VI.

Chemist Corner

(Continued from page 83)

the specific gravity and saponification number are means of checking on whether or not a linseed oil is of the aged type (Table IV).

On the basis of these data it is suggested that a specific gravity determination be used to identify an aged linseed oil if there is any question regarding its type. If the specific gravity is in the range of .948-.958 it can be assumed to be an aged oil. The identification can be confirmed if ne-

cessary by determining the saponification number; however, the specific gravity is a much easier test.

Aged linseed oils Nos. 8, 9 and 10 are the standard products of three different companies and according to information received from these companies are produced to have a specific gravity which is most likely within the suggested range of .948-.958. The tabulation below contains the company name, address, their trade name for the aged oil and their specification data for these oils. The order of the companies does not necessarily coincide with the order of the aged oils listed previously (Table V).

Raw linseed oil is sometimes aged by a blowing process so that an aged oil may be a blown oil but the term "aged" is the one commonly used for specifying this type of oil in the protective coatings industry.

One precaution to be observed is occasioned by the fact that on continued exposure to atmosphere, linseed oil is slowly oxidized. If this oxidation proceeds far enough, its value as a dispersing agent is impaired, but this condition is usually indicated by a change in color from a straw yellow to a greenish-yellow tint. Since aged oil will keep almost indefinitely in a closed container, it is suggested that the stock of oil be kept either in a tightly closed metal or brown glass container and the dropping bottle be cleaned and refilled every few weeks with fresh oil stock.

Summary

When oleic acid is used as a dispersing agent in the turbidimetric determination of the specific surface of portland cement by A.S.T.M. Method C 115-42, the values obtained for specific surface are inconsistent when a trace of moisture is present. These erratic results which are caused by foaming also occur frequently when the relative humidity of the air is high.

Aged linseed oil with a specific gravity of .948-.958 when used as a dispersing agent for cement in kerosene in place of oleic acid is not sensitive to traces of moisture or high humidity laboratory air as evidenced by the fact that no foaming is caused under these conditions and the precision of the specific surface determination is not impaired.

Seeks Dredging Permit

ARKADELPHIA SAND AND Gravel Co., Arkadelphia, Ark., has applied to the Corps of Engineers for a permit to dredge sand and gravel from the Ouachita River near Arkadelphia.

Company	Product Name	Company Specifications
Spencer Kellogg & Sons, Inc. Buffalo, N. Y.	Aged Linseed Oil	Specific Gravity .948-.951 Saponification No. 198-208
Bisbes Linseed Co. Philadelphia, Penn.	Aged Linseed Oil	.948-.958 198-199
John T. Lewis & Bros. Co. Philadelphia, Penn.	Aged Raw Linseed Oil	.948-.958 198-200

Table V: Specification data for aged oil

Effect of Some Inorganic and Organic Compounds On the Solubility, Setting Time and Tensile Strength of

CALCINED GYPSUM

By WALLACE C. RIDDELL*

LITERATURE as far back as the early part of 1900 contains conflicting data on the effect of accelerators and retarders on the physical properties of calcined gypsum, essentially $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$. Welch reviewed this in his paper published in November, 1923.¹

He reviews the chemical process of the setting of plaster and discusses both the "colloidal-gel" theory and the crystallization theory. He also reviews and gives much of the data of Rohland on the effect of accelerators and retarders on the setting time of plaster,² and also the data of Traube³ who published data on the effect of setting time for a large number of both inorganic and organic salts. Fisher recently reviewed the literature in his paper on "The Setting of Gypsum Plaster". He gives the effect of setting time on plaster for the addition of a 0.2 percent solution of several salts, using 200 gr. of "plaster of Paris" and 100 ml. 0.2 percent solution which is equivalent to approximately 2 lb. per ton of added salt. He also gives plots of "Differential Thermal Analysis of Gauged Plaster of Paris."

There has been much discussion as to the effect of change in solubility of $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ on the setting time. Little correlated practical data is available on the effect of added salts on the physical properties of calcined gypsum or plaster. We have determined some of this data and this is given in Table 1. For these tests a sample of calcined gypsum, which analyzed 96.7 percent $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$, 1.10 percent CaCO_3 , 1.5 percent insoluble, 0.30 percent R_2O_3 , was used; 70 percent normal consistency was used for all strength tests; solubility determinations were made at 25 deg. C.; solubility is reported as grams CaSO_4 per 100 ml. solution; setting time tests are somewhat arbitrary but were all made by the same method — using large Gillmore needle with penetration of

needle point to 0.1 cm. For each set of determinations, a sample of the untreated $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ was tested as a control. Salts were added as follows:

0.25 percent = 5 lb. per ton; 0.50 percent = 10 lb. per ton; 0.75 percent = 15 lb. per ton; 1.0 percent = 20 lb.

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Table 1: Setting Time in Minutes; Tensile Strength p.s.i.; Solubility = grams CaSO_4 per 100 ml. @ 25 deg. C. Weight of salt added in grams per 100 grams plaster or percent

Salt Added Grams	0.25	0.50	0.75	1.00	2.00	Plaster Only
NaCl						
Set	22	18	15	10	7	32
Briq. dry wt.	71	70	71	70	68	71
T.S. p.s.i.	255	250	210	200	180	270
Sol. CaSO_4	0.793	0.548	0.953	1.057	1.203	0.754
KCl						
Set	20	15	10	8	5	32
Briq. dry wt.	72	71	72	72	71	72
T.S. p.s.i.	260	260	300	260	280	265
Sol. CaSO_4	0.821	0.559	0.998	0.921	1.073	0.763
NH_4Cl						
Set	20	15	12	10	7	30
Briq. dry wt.	71	70	71	70	69	71
T.S. p.s.i.	280	260	240	230	200	270
Sol. CaSO_4	0.878	0.955	1.269	1.799	1.776	0.770
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$						
Set	30	30	30	25	25	30
Briq. dry wt.	73	71	71	72	74	70
T.S. p.s.i.	290	275	230	235	190	260
Sol. CaSO_4	0.659	0.660	0.624	0.615	0.599	0.771
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$						
Set	30	30	30	30	30	30
Briq. dry wt.	71	72	72	71	72	73
T.S. p.s.i.	270	255	210	190	165	290
Sol. CaSO_4	0.580	0.577	0.554	0.505	0.503	0.760
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$						
Set	30	25	25	25	20	30
Briq. dry wt.	71	72	72	71	72	72
T.S. p.s.i.	290	240	220	200	190	290
Sol. CaSO_4	0.817	0.887	0.948	1.050	1.165	0.752
NaNO_3						
Set	28	23	20	15	12	32
Briq. dry wt.	73	72	72	73	73	72
T.S. p.s.i.	255	270	250	290	290	270
Sol. CaSO_4	0.524	0.897	0.900	0.978	1.112	0.756
KNO_3						
Set	20	20	15	12	8	30
Briq. dry wt.	71	72	71	70	70	72
T.S. p.s.i.	270	250	240	240	230	250
Sol. CaSO_4	0.791	0.856	0.878	0.911	0.974	0.762
NH_4NO_3						
Set	23	20	17	15	12	32
Briq. dry wt.	73	71	71	71	70	72
T.S. p.s.i.	250	210	810	265	210	280
Sol. CaSO_4	0.850	0.952	0.989	1.046	1.225	0.765
$\text{Ba}(\text{NO}_3)_2$						
Set	35	30	30	30	35	35
Briq. dry wt.	72	73	73	72	74	71
T.S. p.s.i.	280	365	360	310	265	280
Sol. CaSO_4	0.729	0.695	0.619	0.614	0.606	0.766
$\text{Ca}(\text{NO}_3)_2$						
Set	35	35	35	37	37	35
Briq. dry wt.	69	69	70	70	70	70
T.S. p.s.i.	255	250	250	225	200	260
Sol. CaSO_4	0.705	0.688	0.659	0.607	0.582	0.768
Na_2SO_4						
Set	20	15	15	10	7	30
Briq. dry wt.	71	71	71	72	71	72
T.S. p.s.i.	265	265	260	245	210	280
Sol. CaSO_4	0.890	0.868	0.685	0.637	0.569	0.762
K_2SO_4						
Set	16	12	10	8	6	32
Briq. dry wt.	71	71	72	72	72	71
T.S. p.s.i.	250	260	270	255	255	260
Sol. CaSO_4	0.706	0.654	0.645	0.599	0.471	0.766
$(\text{NH}_4)_2\text{SO}_4$						
Set	20	15	12	8	6	32
Briq. dry wt.	73	72	72	71	72	78
T.S. p.s.i.	280	275	265	255	260	250
Sol. CaSO_4	0.754	0.737	0.713	0.718	0.667	0.770
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$						
Set	30	25	25	25	20	30
Briq. dry wt.	70	71	70	70	70	71
T.S. p.s.i.	260	290	260	265	245	260
Sol. CaSO_4	0.740	0.732	0.700	0.690	0.705	0.766
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$						
Set	15	15	10	7	7	30
Briq. dry wt.	72	72	71	71	72	72
T.S. p.s.i.	260	265	255	260	265	265
Sol. CaSO_4	0.765	0.765	0.765	0.765	0.765	0.765

*Chemical engineer, Kaiser Gypsum Co., Oakland, Calif.
†P. C. Welch, U. S. Bureau of Standards, Journal of American Ceramic Society, Nov. 1923.
‡Bölling, Zeits. für Elck 14-421-110.
§B. C. Fisher, A.S.T.M. Bulletin, Sept., 1953.

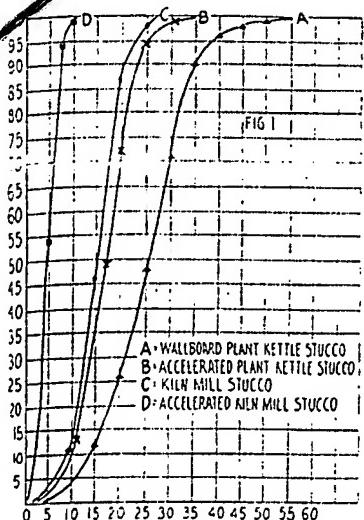


Fig. 1: Rates of rehydration of calcined gypsum made by different methods

Calcined Gypsum Studies

(Continued from page 199)

per ton; and 2.0 percent = 40 lb. per ton of plaster.

Solubility Determinations

Solubility determinations were made by precipitation of either the SO₄ or the Ca ion.

In actual practical use, the acceleration of set of plaster is much more effective than shown in Table I for several of the salts used such as NaCl, KCl, K₂SO₄, (NH₄)₂SO₄, CaSO₄ · 2H₂O (selenite crystals) and salts which hydrolyze with water to give an acid reaction such as Al₂(SO₄)₃, etc.

We have also determined the rates of rehydration of calcined gypsum made by different methods and a few of these results are shown in Fig. 1.

The calorimeter used was a modified old type Parr, and the calorimeter correction was determined with ZnO + HCl, NaOH + HCl and with a pure sample of beta CaSO₄ · ½ H₂O under exactly the same conditions as obtained for the experimental data on rehydration rates, using 100 gr. plaster, 100 gr. distilled H₂O and accelerators as noted; 3-in. immersion thermometers graduated to 0.1 deg. C. and reading glass effective to 0.05 deg. C. The heat of hydration of fine beta CaSO₄ · ½ H₂O is 4600 calories per gram formula weight, equal to 3180 calories per 100 grams. The specific heat of CaSO₄ · 2 H₂O is 0.259 at 25 deg. C. and 0.268 at 40 deg. C. calories per gram.

The calorimeter data was primarily used to measure the rate of rehydration or crystallization of wallboard mixes and the effect of various accelerators. It is an easily applied and quick method for this

(Continued on page 117)

Na ₃ PO ₄	Set	1:15 hrs.	3:00	5:00	10:00	18:00	36 min.
	Briq. dry wt.	72	72	71	71	71	72
	T.S. p.s.i.	180	110	90	70	60	270
	Sol. CaSO ₄	0.863	1.045	1.190	0.935	0.542	0.760
(NH ₄) ₂ PO ₄	Set	1:00	2:00	4:00	7:00	16:00	32 min.
	Briq. dry wt.	71	71	70	71	71	71
	T.S. p.s.i.	215	200	180	170	150	280
	Sol. CaSO ₄	0.456	0.428	0.532	—	0.518	0.759
KOH	Set	15 min.	10	7	5	4	30 min.
	Briq. dry wt.	74	71	72	71	72	72
	T.S. p.s.i.	255	245	245	230	200	270
	Sol. CaSO ₄	—	—	—	—	—	0.764
Ca(OH) ₂	Set	23	20	17	21	21	30
	Briq. dry wt.	71	71	71	72	72	71
	T.S. p.s.i.	280	310	310	300	270	275
	Sol. CaSO ₄	0.736	0.719	0.719	0.720	0.722	0.760
Ba(OH) ₂	Set	30	30	30	35	35	30
	Briq. dry wt.	71	73	73	72	73	71
	T.S. p.s.i.	260	260	255	285	235	280
	Sol. CaSO ₄	—	—	—	—	—	0.776
Na ₂ CO ₃	Set	80	30	30	30	25	32
	Briq. dry wt.	71	72	71	72	70	71
	T.S. p.s.i.	210	75	85	110	90	260
	Sol. CaSO ₄	0.987	1.673	2.120	2.410	3.530	0.753
(NH ₄) ₂ CO ₃	Set	35	37	40	40	50	35
	Briq. dry wt.	68	68	68	66	45	70
	T.S. p.s.i.	195	145	105	60	30	265
	Sol. CaSO ₄	0.892	1.060	1.218	1.405	1.820	0.763
NaHCO ₃	Set	35	40	50	30	25	30
	Briq. dry wt.	70	68	65	58	54	71
	T.S. p.s.i.	230	170	105	80	65	260
	Sol. CaSO ₄	0.862	0.966	1.915	1.728	1.768	0.760
Na ₂ B ₄ O ₇	Set	30	35	40	1:15	7:00 hrs.	32
	Briq. dry wt.	72	73	72	72	79	73
	T.S. p.s.i.	300	295	290	220	155	275
	Sol. CaSO ₄	0.847	0.889	0.890	0.878	0.868	0.769
H ₂ B ₄ O ₇	Set	26	26	28	27	34	30
	Briq. dry wt.	71	72	71	72	71	71
	T.S. p.s.i.	250	250	200	200	190	270
	Sol. CaSO ₄	0.994	1.231	1.399	1.582	2.171	0.763
HCl	Set	10	8	7	5	3	35
	Briq. dry wt.	7.5	7.5	62	61	61	70
	T.S. p.s.i.	158	110	55	65	60	255
	Sol. CaSO ₄	0.994	1.231	1.399	1.582	2.171	0.763
H ₂ SO ₄	Set	22	25	25	20	20	35
	Briq. dry wt.	69	66	62	62	59	70
	T.S. p.s.i.	240	210	185	185	170	260
	Sol. CaSO ₄	0.659	0.548	0.545	0.532	0.465	0.764
NaHSO ₄	Set	25	20	15	10	5	30
	Briq. dry wt.	72	70	70	70	66	71
	T.S. p.s.i.	275	205	210	200	198	260
	Sol. CaSO ₄	0.808	0.753	0.685	0.560	0.465	0.754
H ₃ PO ₄	Set	1:30 hr.	50	50	50	45	35 min.
	Briq. dry wt.	63	61	60	58	54	70
	T.S. p.s.i.	175	170	145	125	120	255
	Sol. CaSO ₄	0.793	0.831	0.870	0.905	1.026	0.764
H ₂ C ₂ O ₄	Set	30	20	20	15	15	35
	Briq. dry wt.	68	70	70	70	69	73
	T.S. p.s.i.	210	235	225	200	200	270
	Sol. CaSO ₄	0.972	1.25	1.55	1.83	2.91	0.762
C ₆ H ₈ O ₇	Set	8:00 hrs.	16:00	16:00	12:00	3:30	82 min.
	Briq. dry wt.	71	73	69	69	56	73
	T.S. p.s.i.	80	80	60	80	50	280
	Sol. CaSO ₄	0.750	0.768	0.764	0.771	0.751	0.748
Ca ₃ H ₅ O ₇	Set	35	40	25	20	20	30
	Briq. dry wt.	73	72	73	72	73	72
	T.S. p.s.i.	245	225	225	270	270	280
	Sol. CaSO ₄	0.796	0.818	0.804	0.827	0.855	0.766
C ₆ H ₈ O ₆	Set	3:00 hrs.	6:00	12:00	24:00	48:00	30 min.
	Briq. dry wt.	73	72	72	71	71	73
	T.S. p.s.i.	270	200	185	170	110	280
	Sol. CaSO ₄	0.755	0.745	0.719	0.712	0.695	0.764
Retarder (1) 36%	Keratin	12:00 hrs.	48:00	7 days	35 days	48 days	32
	Briq. dry wt.	75	74	72	72	73	73
	T.S. p.s.i.	180	175	180	170	No test	280
	Sol. CaSO ₄	0.724	0.716	0.699	0.688	0.678	0.766
C ₆ H ₁₂ O ₆	Dextrin C.P.C. #152	80 min.	30	30	30	80	32
	Briq. dry wt.	71	73	72	72	71	72
	T.S. p.s.i.	810	280	300	280	240	285
	Sol. CaSO ₄	0.709	0.710	0.711	0.715	0.715	0.760
C ₁₂ H ₂₂ O ₁₁	Cane Sugar	Set	32	30	32	35	32
	Briq. dry wt.	72	73	73	73	78	71
	T.S. p.s.i.	275	280	320	325	340	270
	Sol. CaSO ₄	0.756	0.713	0.743	0.744	0.735	0.765

$(\text{CaH}_{10}\text{O}_6)_n$ Starch						
Set	32	32	32	35	35	32
Briq. dry wt.	74	71	72	72	73	73
T.S. p.s.i.	310	280	270	300	305	280
Sol. CaSO_4	0.755	0.756	0.759	0.759	0.764	0.771
$\text{C}_6\text{H}_{10}\text{O}_6$ Glycerol						
Set	35	35	32	35	32	35
Briq. dry wt.	72	69	69	68	66	70
T.S. p.s.i.	280	255	245	240	190	255
Sol. CaSO_4	0.729	0.737	0.744	0.748	0.754	0.764
$(\text{NH}_4)_2\text{CaO}_4$ Am. Oxalate						
Set	22	17	15	11	7	35
Briq. dry wt.	70	71	70	71	70	70
T.S. p.s.i.	240	225	260	250	230	255
Sol. CaSO_4	0.938	1.112	1.292	1.504	2.263	0.763
$\text{NaKC}_4\text{H}_4\text{O}_6$ Rochelle salt						
Set	1:15 hr.	1:00	55	40	35	35
Briq. dry wt.	72	72	69	69	68	72
T.S. p.s.i.	270	270	210	220	230	250
Sol. CaSO_4	0.668	0.960	1.046	1.139	1.534	0.752

Calcined Gypsum Studies

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particular application. It should be noted that for ordinary calcined gypsum, the heat of rehydration of essentially beta $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ can be measured quite accurately up to approximately 98 percent, but as Southard¹ has pointed out the complete rehydration of alpha $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ is a very slow reaction beyond the point of approximately 95 percent hydration.

That the rehydration or setting of calcined gypsum, $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$, to form $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is an autocatalytic reaction can be shown by plotting the solubility of CaSO_4 versus time. This data is shown in Fig. 2 for kettle-calcined gypsum, essentially $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O} + 10$ percent soluble anhydrite, CaSO_4 . The setting time of this material (by Gillmore needle test) was 35 min., and at this time the plot shows the solubility of CaSO_4 at 0.50, or approximately half rehydrated.

The solubility of the calcined gypsum was 0.855 at 25 deg. C., and the

J. C. Southard, U. S. Bureau of Mines, Technical Paper 625.

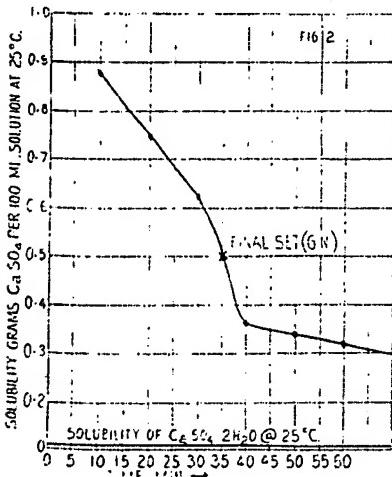


Fig. 2: Solubility of calcined gypsum vs. setting time. Data indicates setting of gypsum is an autocatalytic reaction

noticed, in the case of a simple rotary kiln, that when draft at the hood is low, there is an upflow of air at the low point, and at the upper point an outflow of gas. The reason for this is the hydrostatic head, easily measurable with a sensitive draft gauge. See Fig. 6, "A".

This very thing occurs in part or in full in the case of planetary coolers. Assuming that the temperature of air coming from the coolers is 1000 deg. F. and the difference in height is 15 ft., the difference in draft will be .14 in. w.g. See Fig. 6, "B".

It is through the draft prevailing in the hood that the air is brought in through the cooler, and there must be sufficient draft to confer the required velocity to the air stream to overcome the rather high flow resistance of the units. The units will not function equally. More air will pass through them when at the low point and less while traversing the high position. The flow may be rather sluggish or even completely interrupted when the unit is at the high point. Thorough draft surveys, both gross and micrometric, if interpreted as to cause and result, are not only extremely interesting but almost always prove very profitable and lead toward higher capacity.

Rotary Lime Kilns

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To what extent stratification can occur is demonstrated by Fig. 5, presenting a gas analysis taken across the kiln outlet. The lower the stream, as long as it is not diluted by inleaking air, the higher the CO_2 , and the lower sample taken at E contained more than twice the CO_2 of the upper sample taken at B. As the source of CO_2 was the limestone, it would have been far heavier than the upper stream of gases on just this account.

In addition to this, and particularly in the preheating zone where the stone is cold, the lower stream will be cooler, an additional reason for being heavier than the upper stream. It is desired to have the hot gases contact the stone which is as unreasonable to expect as that light oil should supplant heavier water in a bottle.

A further belief exists that, particularly at low kiln capacities, there is a counterflow. The low heavier stream of gases flow part way at least down rather than up the kiln. This frequently occurs in ducts where the thermal head out-balances the velocity head.

Another case concerns the planetary lime coolers. It may be frequently

Gypsum Production

DOMESTIC MINE PRODUCTION of crude gypsum amounted to 7,909,386 short tons in 1953, or 2 percent below the 8,070,079 tons reported for 1952, as reported by the Bureau of Mines. Production gains and losses among the gypsum products were irregular, with marked gains being shown for sanded plaster, other building plasters, plate glass and terra-cotta plasters, fillers and unclassified uncalled products, and sheathing board, while prepared finishes were down 17 percent and several other building products down as much as 9 percent. Lath production increased 5 percent; wallboard and laminated board increased 9 percent.

	Short Tons	
	1953	1952
Crude gypsum:		
Mined	7,909,386	8,070,079
Imported	3,191,732	3,067,905
Calced gypsum produced	7,178,200	6,870,161
Gypsum products sold or used:		
Uncalced uses:		
Portland cement retarder	1,819,401	1,693,074
Agricultural gypsum	541,430	583,492
Fillers and unclassified	26,624	23,278
Industrial uses:		
Plate-glass and terra-cotta	61,171	48,577
Pottery plasters	43,958	43,991
Dental and orthopedic plasters	10,638	11,037
Other industrial uses	138,339	148,938
Building uses:		
Plasters:		
Base-cast	1,727,136	1,904,260
Sanded	300,567	180,047
To mixing plants	11,437	11,583
Gauging and molding	168,529	176,941
Prepared finishes	12,098	14,544
Other building plasters	824,422	220,447
Keene's cement	49,033	52,593
Lath	2,485,307	2,814,555
Wallboard	3,598,755	3,312,544
Sheathing	181,193	117,381
Tile and miscellaneous	26,649	27,044

*M sq. ft.